

By

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3. Polymers

1.What are polymers? What is polymerization? Give examples.

Polymers are important engineering materials. Polymers have diversified uses in day-to-day life. Natural polymers, such as polysaccharides, cellulose starch proteins, have been parts of every living being since the beginning of life. In addition, there are numerous man-made polymers, which have a wide range of applications.

Polymers are made of two Greek words ‘poly’ means many and ‘mers’ means unit or part. A polymer is a high molecular weight compound formed by the joining of a large number of small units. The process of joining together of a large number of simple small molecules to form very big molecules is termed as polymerization. Small molecules that combine with each other to form a polymer are known as monomers, e.g. polystyrene and polyethylenes

A polymer that is obtained from only one type of monomer is known as homo polymer. On the otherhand polymer obtained from different type of monomers is referred to as copolymer.

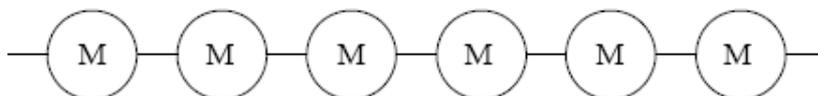
2) Describe the classification of polymers?

Polymers can be classified into several ways.

(a).Based on Structure of Polymers

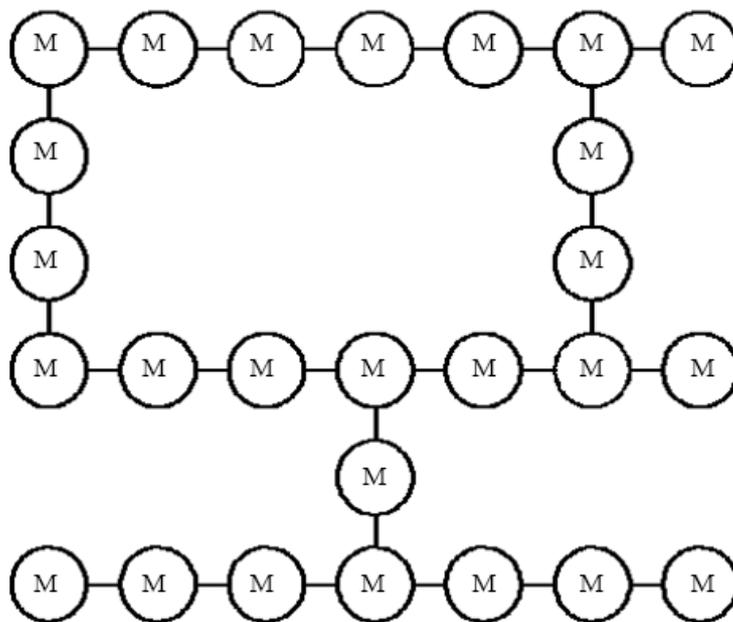
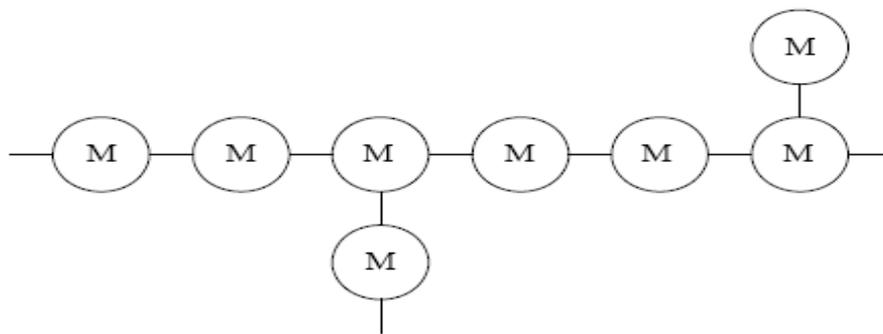
On the basis of the structures, polymers can be classified into three groups.

1. *Linear chain polymer:* In these polymers, monomers are joined together in a chain. They have high density and high melting point due to the well-packed structure, e.g. polyethylene and nylon.
2. *Branched chain polymer:* In these polymers, the chain of the polymer contains branches of monomers, which hinders the close packing of polymeric chains, and, hence, are less tightly packed in comparison to the linear chain polymers. They have low melting points and less density in comparison to the linear chain



M = Monomer

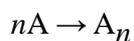
3. *Crosslinked polymers:* In the crosslinked polymers, monomers are cross- linked together in all the three dimensions. Eg.Bakelite.



(2) Based on Types of Monomers

On the basis of monomers, polymers are classified into two groups:

1. *Homopolymer*: It is formed by the polymerisation of one type of monomers.

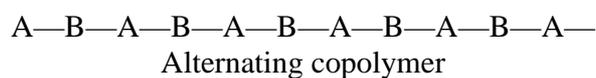


where A is a monomer.

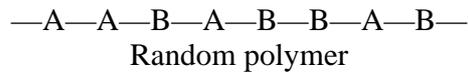
For example, polyethylene and PVC.

2. *Copolymer*: When two different types of monomers are joined in the same polymeric chain, the polymer is called a copolymer. Let us consider two different monomers A and B that can be joined together in many different ways.

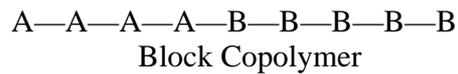
When the two monomers are arranged in an alternating fashion, the polymer is called an alternating copolymer.



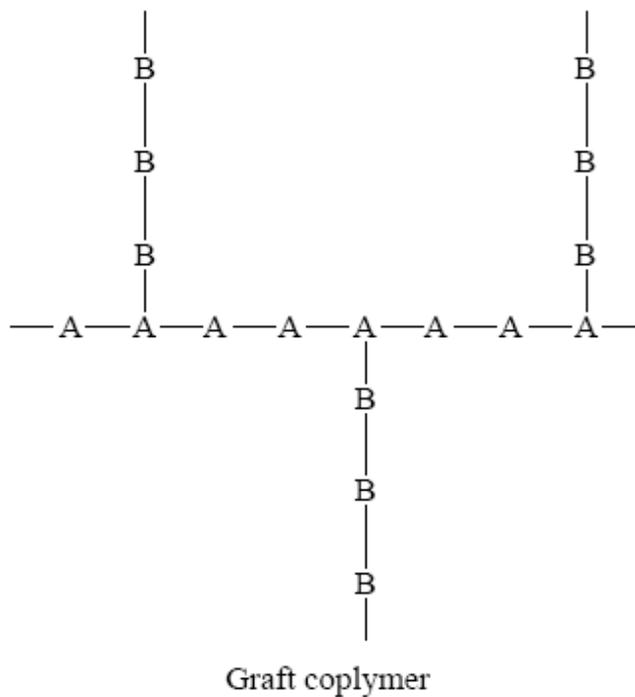
In the random copolymer, the two monomers may follow in any order.



In a block copolymer, the same types of monomers are grouped together and the different types of monomers are grouped together.



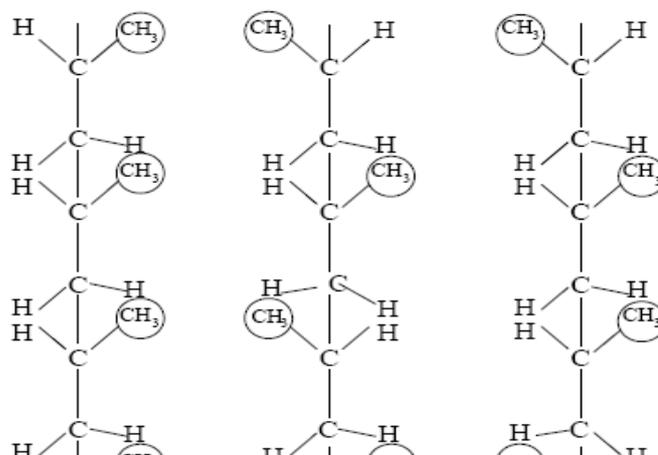
When chains of a polymer made of monomer B are grafted on to a polymeric chain of monomer A, graft copolymer is obtained.



(3) Based on Tacticity (Configuration)

There are three different types of polymers depending upon the relative geometric arrangement of the functional (side) groups.

1. *Isotactic polymer*: All the functional groups are on the same side of the polymer chain.
For example



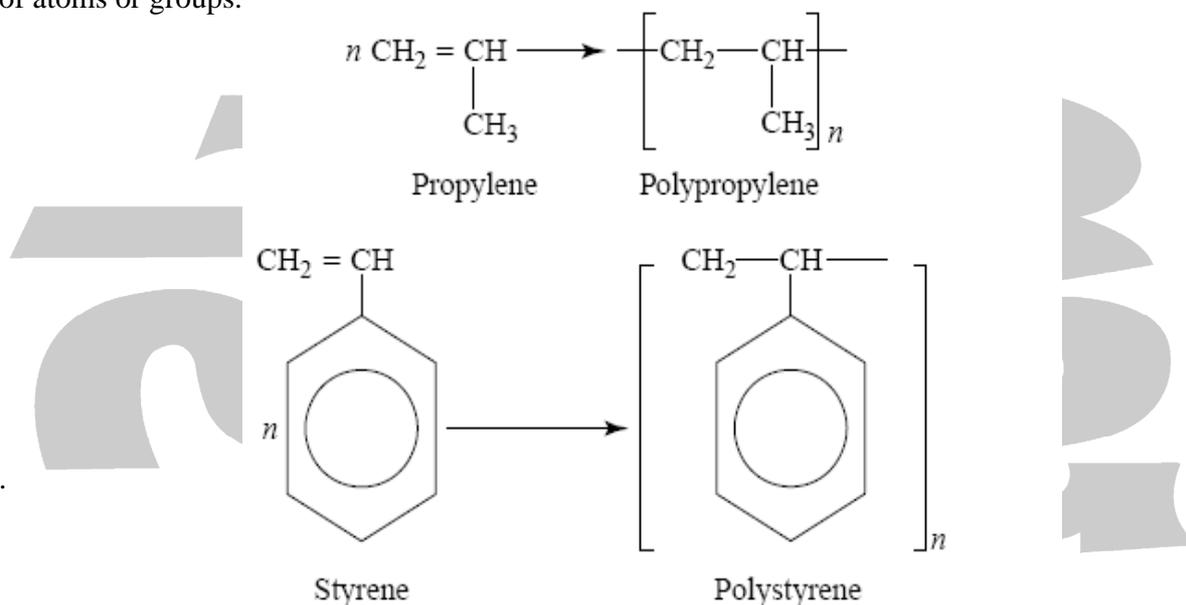
2. *Syndiotactic polymer*: All the functional groups are arranged in regular on alternate sides of the polymeric chain.
3. *Atactic polymer*: All the functional groups are arranged randomly on both sides of the polymeric chain.

(4) Based on Synthesis

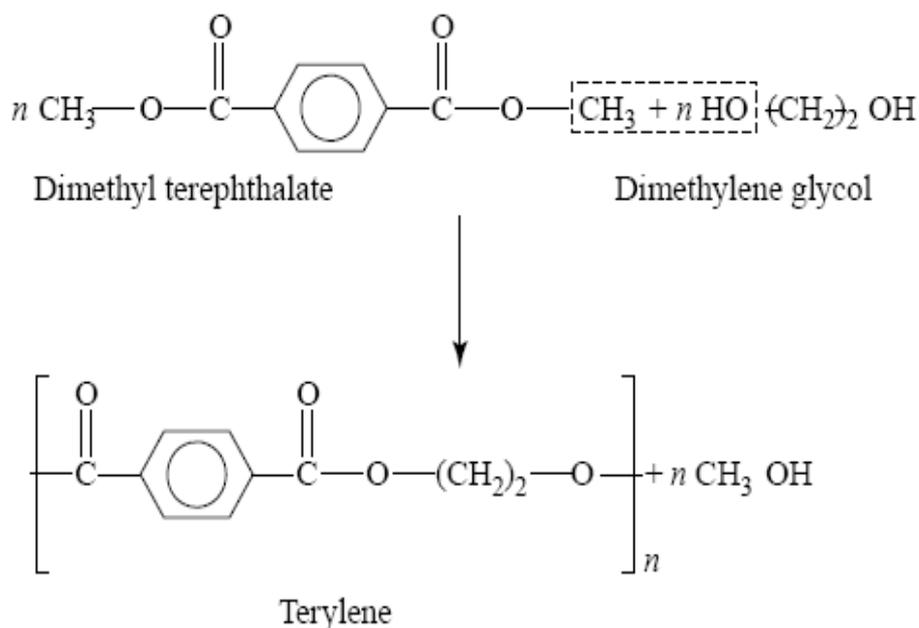
On the basis of the synthesis, polymers are of two types:

- (i) addition polymers and
- (ii) condensation polymers.

Addition Polymers: These are formed by the polymerisation of monomers without the elimination of atoms or groups.



Condensation Polymers: These are formed by the polymerisation of monomers with the elimination of small molecules such as NH_3 , H_2O , CH_3 and OH



3) Explain Addition polymerisation. Give examples?

Addition Polymerisation (Chain Growth Polymerisation)

Addition or chain growth polymerisation is the linking of molecules having multiple bonds. These unsaturated monomers have extra internal bonds which are able to break and link up with other monomers to form repeating chain. All the addition polymers are chain growth polymers, but few examples of condensation polymers are also present those mechanism proceed through chain growth polymerisation.

Mechanism: Addition polymerisation proceeds in three important steps:

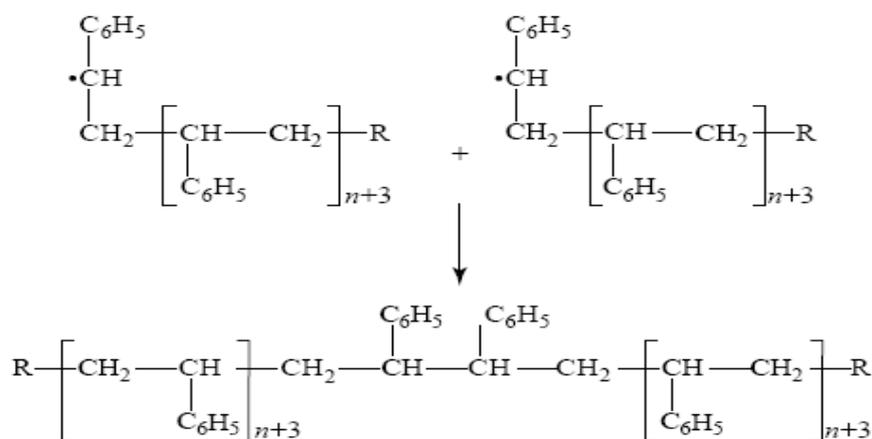
1. *Initiation step:* This step involves the formation of a reactive particle.
2. *Propagation step:* It consists of a growing polymer chain having reactive particles.
3. *Termination step:* In this step, the growth of the chain is finally terminated.

The following three different types of reactive particles have been found to be formed during the addition polymerization: (i) free radicals, (ii) carbocation and (iii) carbanion. So on the basis of these reactive species, addition polymerization is classified into the above three categories.

4. What is free radical polymerization? Explain the steps involved in free radical polymerization?

Free Radical Polymerisation

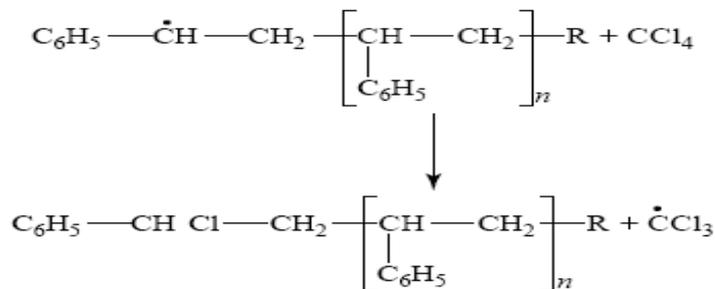
In the free radical polymerisation, monomer is activated by the action of light, heat, or by adding



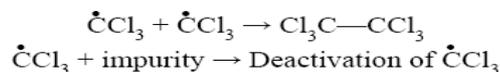
(b) *Reaction with inhibitors:* Polymeric chain can be terminated by the reaction of inhibitors, such as hydroquinone phenol, amines, etc. For example, phenoxy radicals ($\text{Ar}\dot{\text{O}}$) derived from phenol (ArOH) are highly resonance stabilized and so unreactive that they cannot initiate chain reaction and thus, polymeric chain is terminated.



c) *Reaction with the solvent:* The solvent molecule, such as CCl_4 , reacts with the Radical and produces CCl_3 radical.



The $\dot{\text{C}}\text{Cl}_3$ radical may then undergo either of the following reactions.



5. Write an account on ionic addition polymerisation

Addition polymerisation reactions, which proceed via ions, may be cation or anion, are known as ionic addition polymerisation. Ionic polymerisation proceeds due to the presence of catalysts and, hence, it is called catalytic polymerisation. Depending upon the type of ion involved, ionic polymerisation is of the following two types: (i) cationic polymerisation and (ii) anionic polymerisation

Cationic Polymerisation (Carbocation Polymerisation): In cationic polymerisation, the catalysts used are Lewis acids (electron acceptor), such as SnCl_4 , TiCl_4 , AlCl_3 , BF_3 and

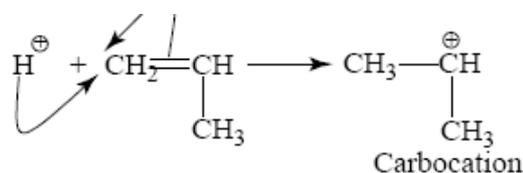
H_2SO_4 . If the catalyst is not a strong protonic acid then the co-catalysts are required to provide protons. The polymerisation proceeds through the formation of the carbocation and the chain growth is accompanied with the transfer of the positive charge along with the polymer chains. Its mechanism involves the following steps:

Step I: Chain Initiation

If the acidic catalyst is not a protonic acid then the co-catalyst is used to produce proton.

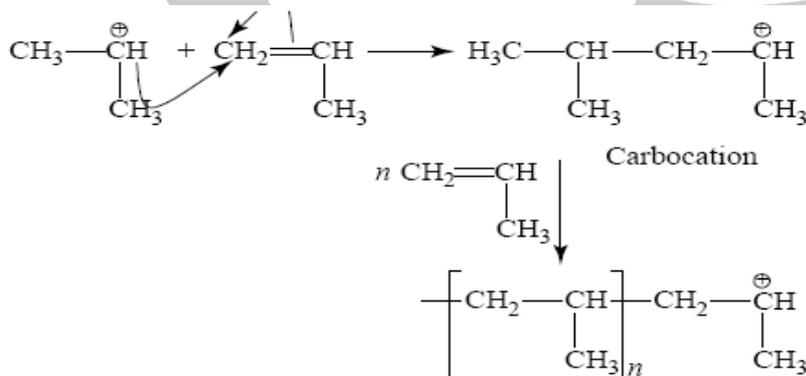


The produced proton adds to the multiple bond of the monomer molecule and forms the carbocation.



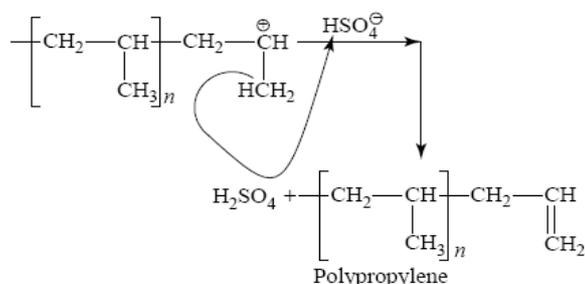
Step II: Chain Propagation

The carbocation reacts with another monomer molecules and chain growth takes place.



Step III: Chain Termination

Chain termination can take place by the combination with an anion or by loss of a proton.

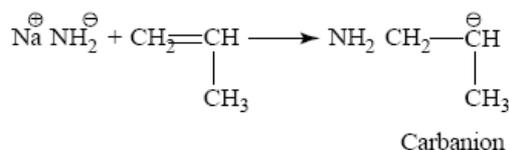


The essential feature of these polymerisations is that they take place at very high rates even at low temperature, e.g. polymerisation of isobutene is completed in a few seconds at -100°C .

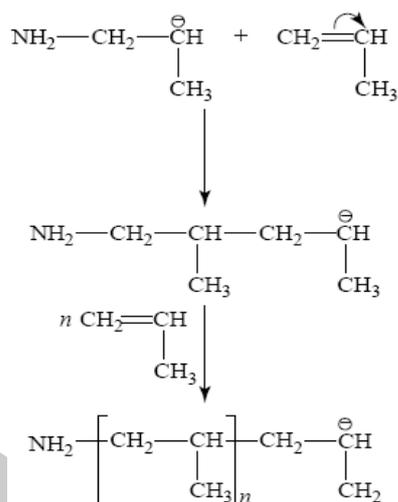
Anionic Polymerisation (Carbanion Polymerisation): Anionic polymerisation involves the formation of carbanion. In these polymerisations, the electron-donor catalysts are used, e.g.

alkali metal alkyls, alkali metal amides and Grignard reagents.

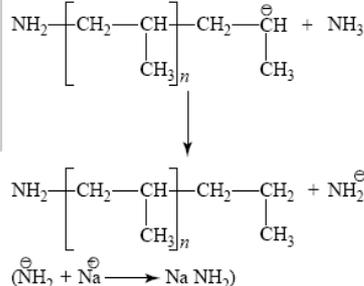
Step I: Initiation Step



Step II: Propagation Step



Step III: Termination Step



Anionic polymerisation is more favourable with the monomers having electron- withdrawing substituents (e.g. CN^-), since such groups help in the stabilisation of the intermediate anion.

In case of anionic polymerisation, if some other molecule or an impurity is not added, termination step cannot take place. Reaction stops, when all monomer is consumed. Hence, polymers produced by this method retain active centres at the end of the chain. Such polymers are known as living polymers. These living polymers may further react with the additional monomer molecule and may be killed by the addition of a terminating agent. So this type of polymerisation may lead to polymers of desired low molecular weight.

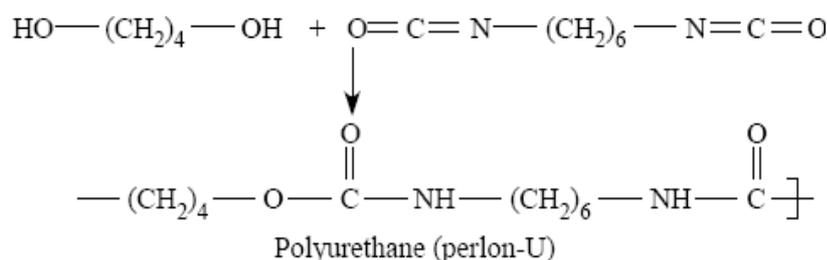
Derivatives of acrylonitrile, acrylic and methacrylic esters, ethylene, styrene and butadiene are the common examples of the monomers polymerised by an- ionic polymerisation reaction.

6.What is step growth polymerization? Explain with an example.

Condensation Polymerisation (Step Growth Polymerisation)

Step growth polymerisation is defined as the polymerisation in which polymers are

formed by the stepwise reaction between functional groups of monomers. Step growth polymers increase in molecular weight at a very slow rate. Mostly condensation polymers are formed by step growth polymerisation but few exceptions also exist. For example, polymerisation of polyurethane (addition polymer) proceeds through step growth mechanism.



In the step growth polymerisation, the monomer disappearance is very fast while in chain growth polymerisation, it is slow. The functionality of the monomer must be two or more than two. The reactions are not exothermic. The molecular weight of the polymer is not the sum of the molecular weights of the monomers.

7) What are the differences between addition and condensation polymerisation?

Difference between addition and condensation polymerization:

Addition Polymers	Condensation Polymers
<ol style="list-style-type: none"> 1. It is also known as chain growth polymerisation 2. It takes place only in monomers having multiple bonds 3. It takes place without elimination of simpler molecule 4. High molecular weight polymer is formed soon. 5. The product obtained by this Polymerization is thermoplastic. 6. Long reaction time give high yields, but molecular weight of polymer is affected slightly. 7. Polyethylene, polystyrene, polypropene, polyvinyl chloride etc. are its examples 	<ol style="list-style-type: none"> 1) It is also known as step growth Polymerization 2) It takes place in monomers having reactive functional groups. 3) It takes place with elimination of simple molecule like H₂O, NH₃, HCl etc. 4) The molecular weight of polymer increases steadily throughout the reaction. 5) The product obtained in the polymerisation may be either thermoplastic or thermosetting plastic 6) Long reaction times are essential to obtain high molecular weights 7) Bakelite, urea formaldehyde resin, epoxy resins, etc. are its examples

8) How polymers are classified based on thermal processing?

On the basis of thermal processing behaviour, polymers may be classified in two groups.

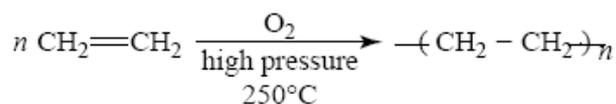
- 1. Thermoplastic Polymers:** Thermoplastics are polymers that soften on heating and become hard on cooling. These are the polymers in which intermolecular forces of attraction are moderate and there are no cross-links between the chains, e.g. polyethylene, polypropylene, PVC nylon-66.
- 2. Thermosetting Polymer:** On heating, extensive cross-link is formed in these polymers between the polymeric chains and, thus, they become hard, e.g. bakelite, urea-formaldehyde terylene.

9) Explain the differences between thermoplastic and thermosetting polymers:

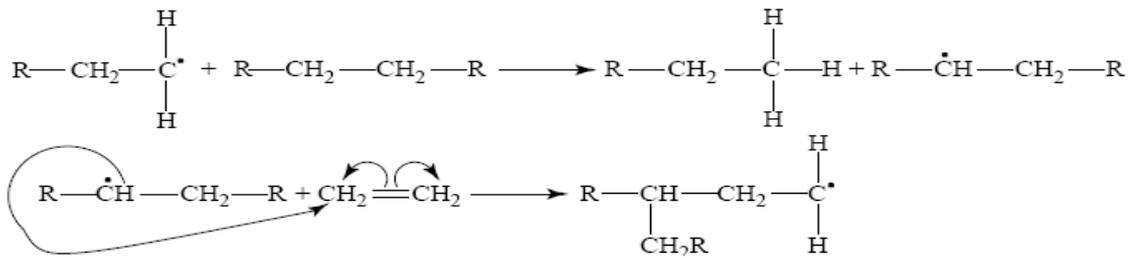
Thermoplastic polymers	Thermosetting polymers
1. On heating, they become soft.	1. They do not soften on heating and become hard. On prolonged heating, these start burning.
2. These can be remoulded or reshaped.	2. They cannot be remoulded.
3. These have linear structures.	3. They have 3D crosslinked structures.
4. They are formed by addition polymerisation.	4. They are formed by condensation polymerisation.
5. They are less brittle and are soluble in organic solvents, e.g. PVC, teflon and nylon.	5. They are more brittle and are insoluble in organic solvents, e.g. bakelite and terylene.

10) Write notes on preparation, properties and uses of polyethylene, poly propylene, PTFE and Poly styrene ?

- 1. Polyethylene (polyethene):** Polyethene is one of the most common polymers. It is used for varieties of products, such as polyethylene bottles, polyethylene bags, sheets, dishes and coatings on milk cartons. The widespread use of this polymer is due to the low cost of the starting materials. Polyethylene (PE) is of two types:
 - (a) Low-density polyethylene (LDPE):** LDPE is polymerised at high pressure of 5000 atmospheres and at a temperature of 250°C in the presence of O₂ as free radical inhibitor.



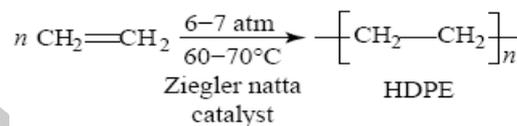
Chain-transfer steps result in the formation of branched polymers.



The presence of branches in the polyethylene molecules does not allow it to pack close together, and hence, its density is low (0.91–0.94 gm/cc) and is known as low-density polyethylene.

LDPE is chemically an inert, a poor electrical conductor and is used in films for packing, toys, insulation wires, pipes, etc.

(b) High-density polyethylene (HDPE): It is polymerised under 6–7atmospheric pressure at 60–70°C in the presence of Ziegler–Natta catalyst ($\text{AlEt}_3 + \text{TiCl}_4$) dispersed in an inert solvent.

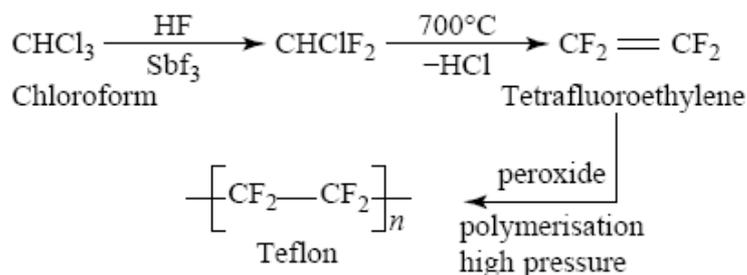


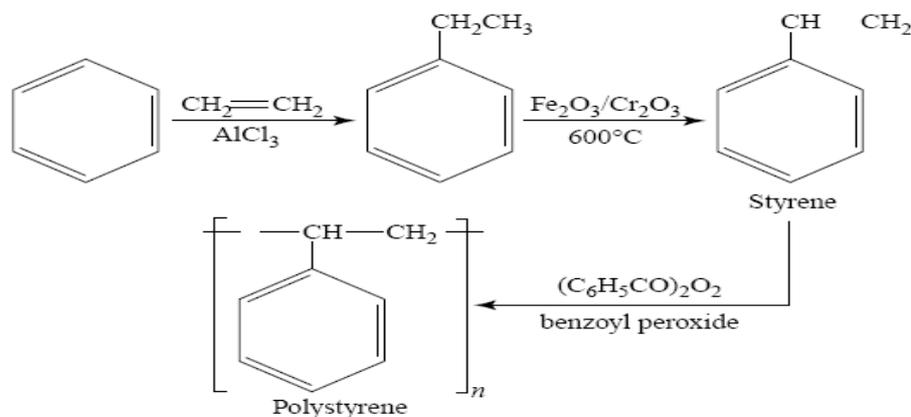
The polyethylene molecules produced by these methods are linear; the ratio of the side chain to the main chain is less than 1/200. Since, the linear molecules can pack themselves, the density of these polyethylene molecules is high (.95–.97 gm/cm³). HDPE is also chemically inert but they are more stiffer and harder than LDPE. They are used in toys, pipes, bottles and in bags for packing. Becasue of its excellent insulation port- eries, it is used for wire and cable coating.

2. **Polypropylene:** It is prepared by passing propylene through Ziegler–Natta catalyst ($\text{AlR}_3-\text{TiCl}_4$) at 100°C at 10 atmospheres.

The polymerisation of propylene is a coordination polymerisation, which produces isotactic polymer with density of 0.905 gm/cm³. Its highly crystalline structure produces a high melting point, stiffness, strength and hardness. It is used in the manufacture of housewares, medical equipment, electronic components, toys, pipes, etc. It is also used as an electrical insulator and as coating on electrical wires.

3) **Polytetrafluoroethylene (Teflon) (PTFE):** It is prepared by the polymerisation of tetrafluoroethylene under pressure in presence of free radical initiator (benzoyl peroxide).





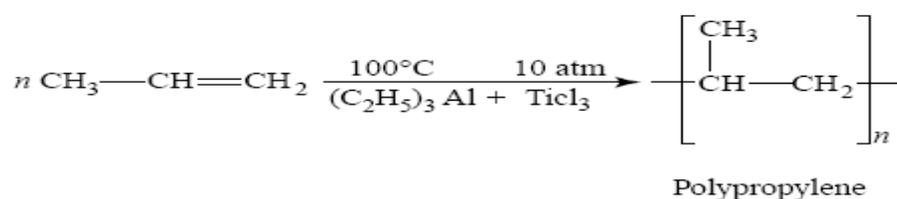
Teflon is also known as fluon

Because of the presence of highly electronegative fluorine atoms, there are strong attractive forces between the different chains in the teflon molecules. This strong attractive force is responsible for high toughness, high chemical resistance towards all chemicals except hot alkali metal and hot fluorine.

It is used in making seals and gaskets, which have to withstand high temperature. It is also used for insulation of electrical items and for making non-stick surface coating, particularly for cooking utensils.

3. **Polystyrene (Styron):** Polystyrene is obtained by free radical addition polymerisation of styrene in the presence of benzoyl peroxide

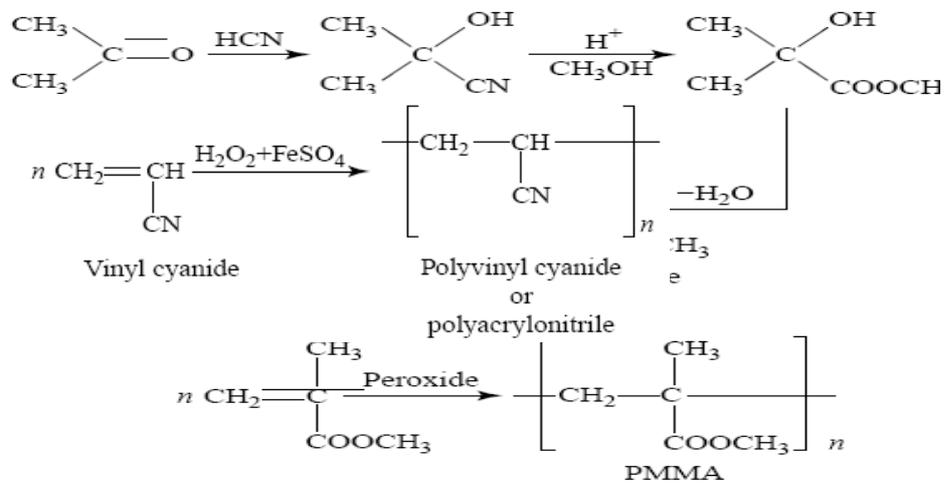
Polystyrene is a linear, transparent, soluble, thermoplastic polymer. It is resistant to alkalies and halogen acids but it can be nitrated and sulphonated by corresponding acids. Polystyrene is used in manufacturing caps for bottles, toilet articles, refrigerator parts, small radio cabinets, brushes, combs, soft drink bottles, etc.



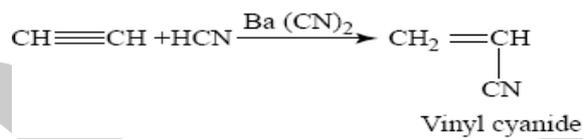
11. What is plexi glass? How is it prepared? Give

characteristics, properties and uses of plexi glass?

Polymethyl Methacrylate (PMMA): It is obtained by polymerisation of methyl methacrylate (MMA) in the presence of organic peroxide. The starting material MMA is obtained from acetone in the following way.



PMMA is also known as plexiglass or Lucite.



It has lightweight and can be moulded almost to any desired shape, the scratching on this can be removed easily by rubbing with solvent such as acetone. So it is the best alternative to glass. Also, optical clarity is the main feature of this polymer. It is used for making optical lenses, aircraft windows, plastic jewellery, etc.

12. What is polyacrylonitrile? How is it prepared? write its applications?

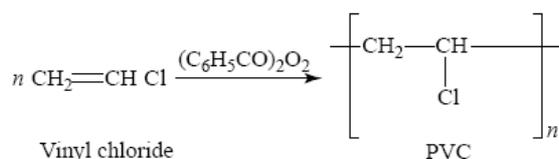
It is prepared by polymerisation of acrylonitrile (vinyl cyanide) in the presence of ferrous sulphate and hydrogen peroxide.

This is also known as orlon or acrilan. The monomer vinyl cyanide is obtained by the reaction of HCN on acetylene in the presence of $\text{Ba}(\text{CN})_2$

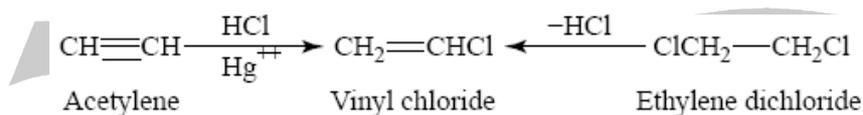
Because of the presence of highly polar cyanide group it has excellent heat resistance capacity. This polymer can be used as wool substituent. It is used for clothes, carpets, blankets, etc.

13) Give an account on preparation, properties of PVC?

Polyvinyl Chloride (PVC): It is obtained by heating vinyl chloride in an inert solvent in the presence of benzoyl peroxide.



The parent compound, vinyl chloride, may be prepared by the following two methods.



PVC is also known as koroseal. Its plasticity can be increased by the addition of a plasticiser (ester of phthalic acid). It is used in making sheets, pipes, rain coats, hand bags, table clothes, plastic dolls, floor covering and electrical insulation, coating on electrical cables.

14. What are poly amides? Write about Nylons?

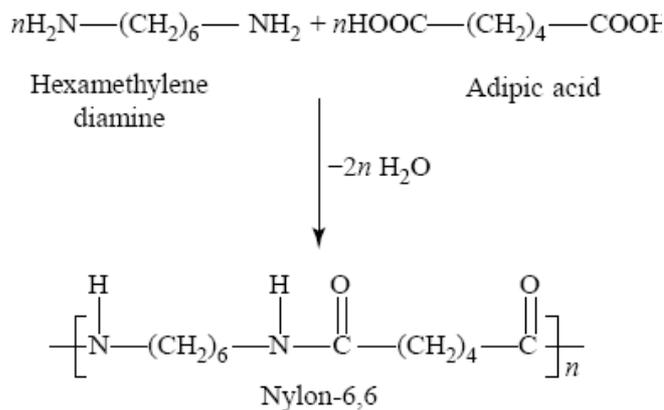
Polyamides: Polyamides are polymers obtained by the condensation polymerization

The first number used in the suffix with the name of nylon represents the number of carbon atoms present in the amine monomer and the second number represents the number of the carbon atoms presents in the acid monomer, e.g. in Nylon-6,10, the six carbon atoms present in the amine and ten carbons present in the acid.

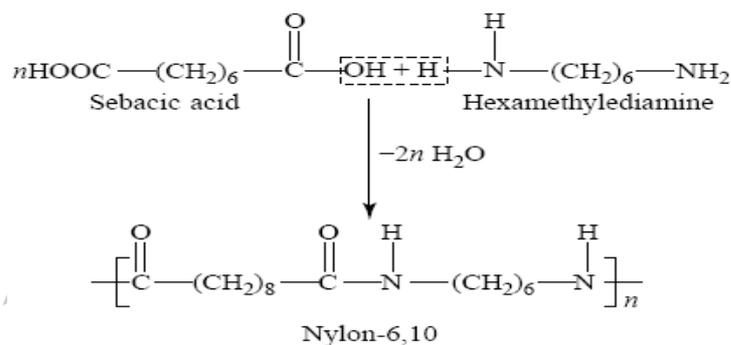
Nylon-6 (Perlon L): It is prepared by the prolonged heating of caprolactum at

260–270°C. Caprolactum is obtained by Beckmann rearrangement of hexamethylene diamine and adipic acid .

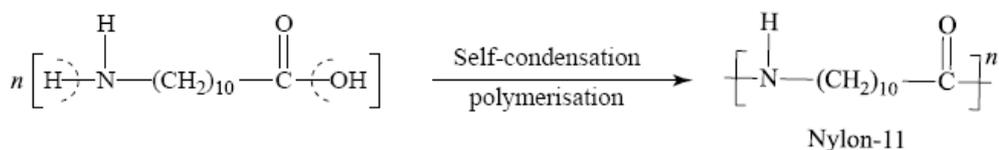
Nylon-6,6: It is obtained by the condensation of hexa methylene diamine and adipic acid. In 1:1 ratio.



Nylon-6,10: It is prepared by the condensation polymerisation of hexamethylene diamine and sebacic acid.



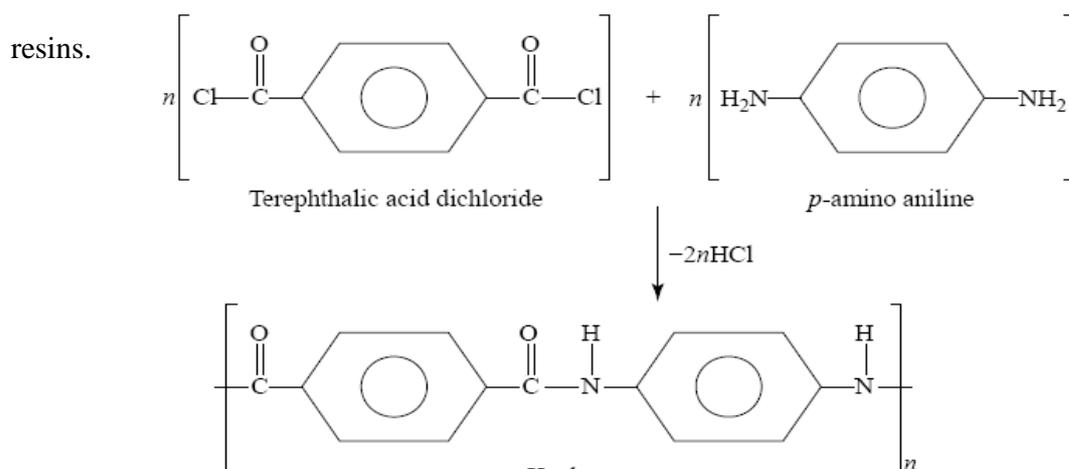
Nylon-11: It is prepared by the self-condensation polymerisation of the amino undecanoic acid.



Nylons are insoluble in common solvents and dissolves only in phenols and formic acid. They possess high temperature stability and high melting point. They absorb little moisture and, thus, are of 'drip-dry' nature. They are used in making socks, undergarments, carpets, tyre cords, ropes, etc. Nylon can be blended with wool.

Kevlar: In Nylon when aliphatic chain is replaced by benzene ring, an aromatic polyamide is formed which is known as Kevlar. It is prepared by the polycondensation between aromatic dichloride and aromatic diamine. Kevlar is stronger and more rigid than the nylons due to the presence of benzene rings. It is used in making car parts, tyres, cables, motorcycle helmets and other high performance materials. It has high heat stability.

It is very important that in order to form thermosetting polymers, at least one of the monomers must have more than two functional groups because if both the monomers possess two functional groups, a linear polymer is formed which will be thermoplastic in nature.



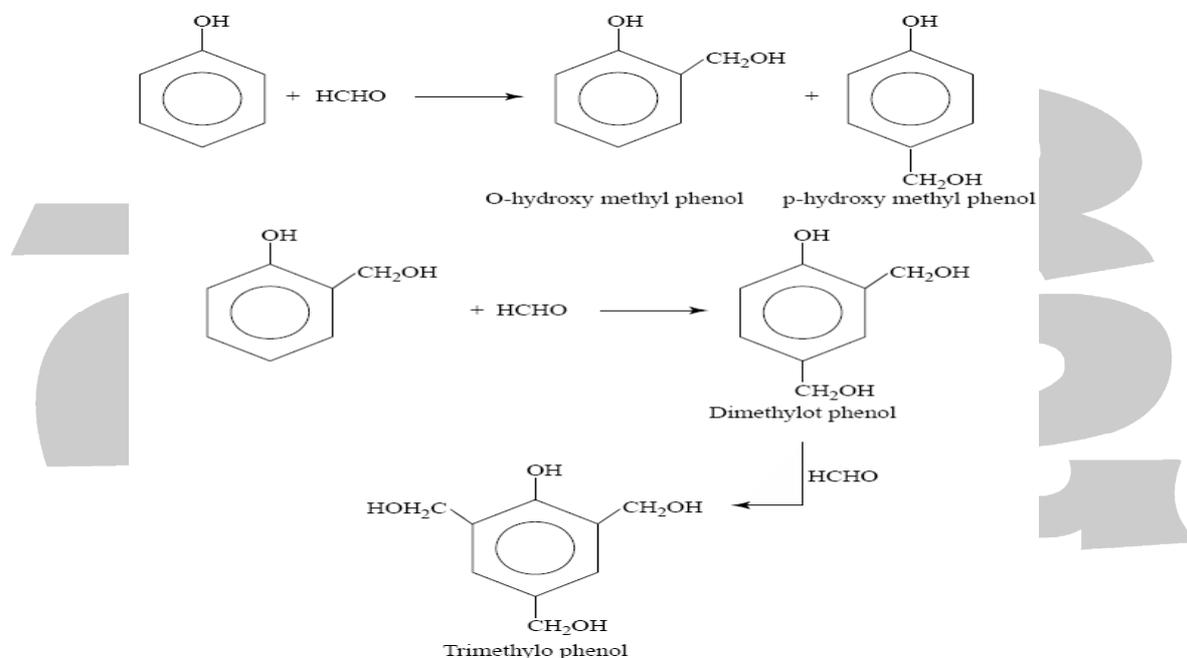
15) .What are phenol-formaldehyde resins? How they are prepared?

Phenolic Resins (Phenoplasts): In these resins, one of the monomers is always phenol molecule. The important phenolic resins are phenol form- aldehyde resins and phenolfurfural

Phenol formaldehyde resins (PF): These are the condensation product of phenol and formaldehyde in the presence of an acid or a base catalyst.

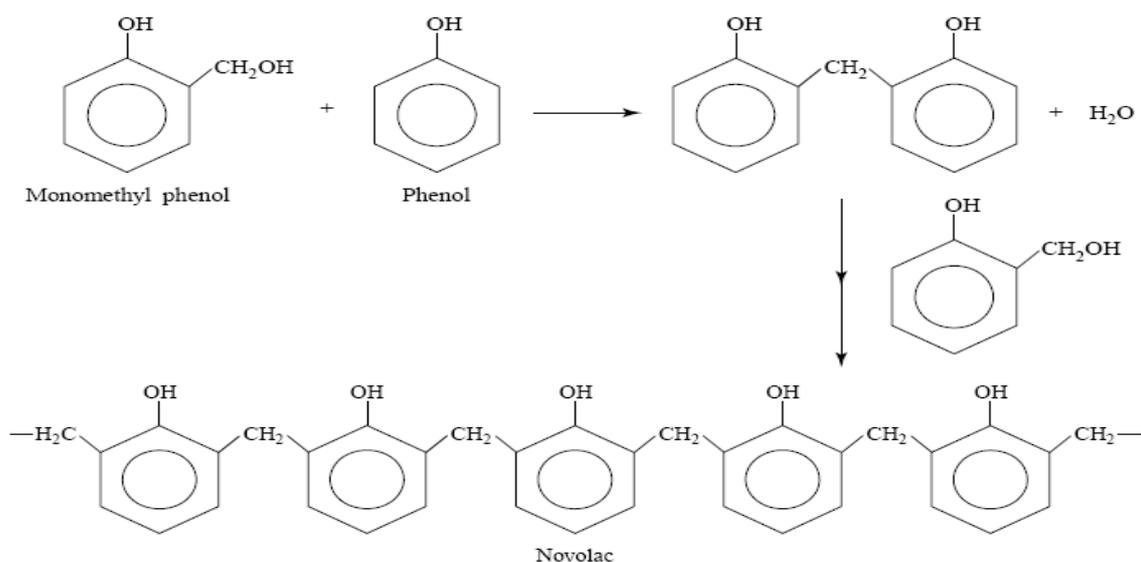
The initial reaction results in o- and p-hydroxy methyl phenol.

In the second stage the monomethylol phenol and di and tri methylol phenols are heated to produce two types of straight chains by condensation of the methylol group and hydrogen atom of benzene ring or another methylene group.



The nature of the product formed depends upon two factors: (i) the proportion of the reactants (phenol and formaldehyde) and (ii) the nature of the catalyst (acidic or basic).

- (a) **Novolac Formation:** When phenol and formaldehyde are heated in the excess of phenol ($P/F > 1$) with an acid catalyst, such as HCl, H₂SO₄ or oxalic acid, a linear polymer is formed which is thermoplastic in nature and is known as Novolac.



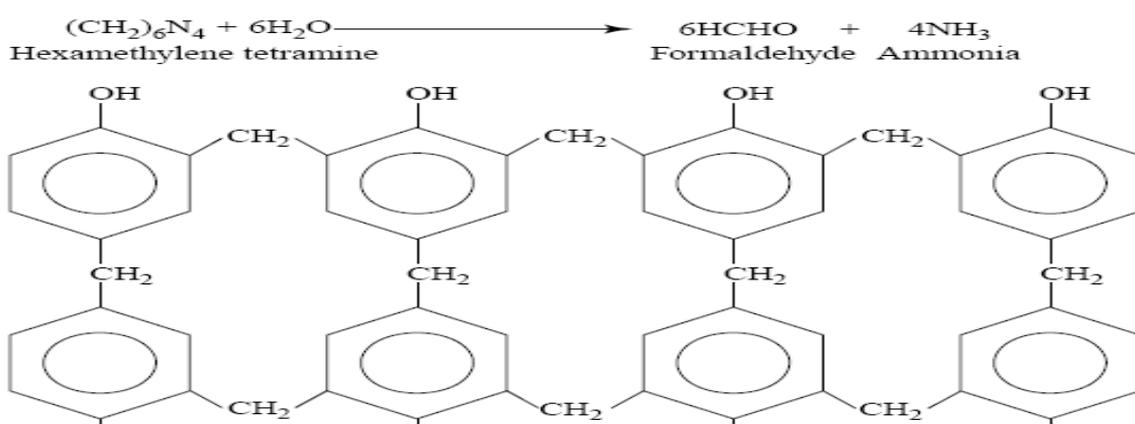
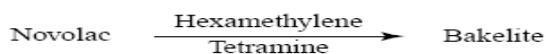
(b)

(c)

(d) **Resole Formation:** When phenol and formaldehyde are heated in the excess of formaldehyde ($P/F < 1$) with basic catalyst, such as Na_2CO_3 , a cross-linked thermosetting resin is formed which is known as Resole.

16. How bakelite is prepared? What are its uses?

Bakelite: On further heating, in the presence of hexamethylene tetramine, Novolac produces 3D cross-linked networked thermosetting polymer which is known as bakelite. The hexamethylene tetramine decomposes into formaldehyde and ammonia, which is used as catalyst and HCHO decreases the P/F ratio as 0.8.



■ Bakelites are hard, rigid and withstand very high temperature and, hence, are used in

Bakelite is used in missile nose cones. They have very good electrical insulating character. Because of their good dielectric properties, they are widely used in electrical, automotive, radio and TV parts. They are also used in paints and varnishes as hydrogen-exchanger resins in water softening.

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