1. POLYCONDENSATION

In polycondensation, the reaction proceeds between monomers containing two or more reactive functional groups (e.g., hydroxyl, carboxyl and amino) condensing with each other. The main features regarding polycondensation are:

(i) To proceed the polymerisation, monomers should have two reactive functional groups.

(ii) The polymerisation takes place by step-wise reaction between reactive functional groups.

(iii) Only one type of reaction (e.g., condensation reaction in this case) between two functional groups is brought about in polymer formation.

(iv) The polymer formed still consists of both the reactive functional groups at its chain end, this is 'active' and not' dead', as in chain polymerisation.

In polycondensation, basic reactions are the same as between various reactive functional groups in low molecular weight organic compounds. Some examples are:

(i) Reaction between a hydroxyl group and a carboxylic group gives an ester and a water molecule. It should be noted that in this reaction, both the functional groups are consumed and forms an unreactive ester functional group, which can not react further with any other monomer molecules.

$$CH_3OH + HOOC\text{-}CH_3 \longrightarrow CH_3COOCH_3 + H_2O$$

Methyl alcohol (one hydroxyl group) | Acetic acid (Carboxylic group) | Methyl acetate (ester group)

(ii) In another example of polycondensation reaction, ethylene glycol reacts with acetic acid and forms ethylene glycol monoacetate. This product still consists of another -OH group which can further react with another molecule of acetic acid. In this case, two molecules of water are liberated and the product contains two ester groups:

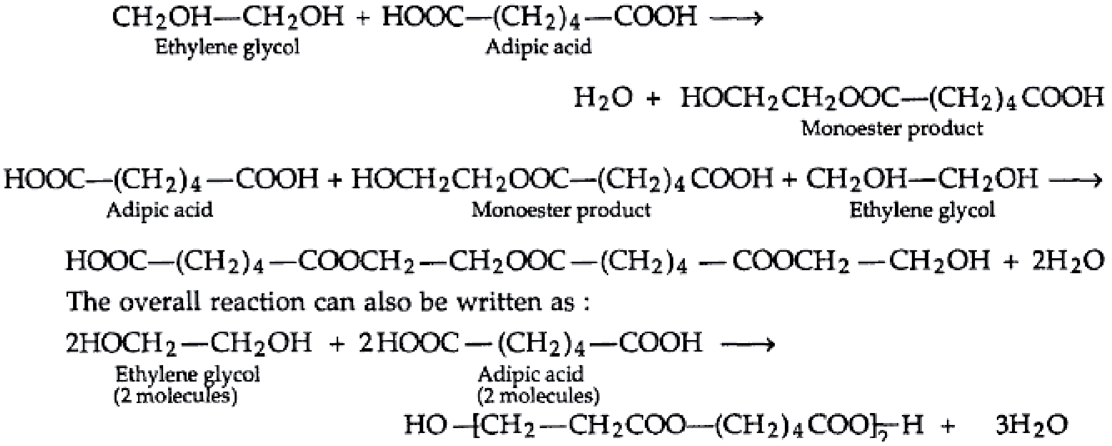
$$CH_2OH\text{-}CH_2OH + HOOC\text{-}CH_3 \longrightarrow HOCH_2CH_2OOCCH3 + H_2O$$

Ethylene glycol (2 hydroxyl groups) | Acetic acid (1 carboxyl group) | Ethylene monoacetate glycol

$$HOCH_2CH_2OOCCH_3 + CH_3COOH \longrightarrow CH_3COOCH_2CH_2COOCH_3 + H_2O$$

Ethylene glycol diacetate

(iii) In this case, two molecules each of ethylene glycol and adipic acids are taken for the polycondensation reaction and form a monoester in first step. This product still consists of two reactive groups, i.e., one hydroxyl and one carboxyl, which can further react with one more molecule of ethylene glycol or adipic acid and gives a diester. This product contains at its ends one hydroxyl and one carboxyl group, which can again react with fresh molecule of ethylene glycol and adipic acid resulting in an bigger molecule. Hence, four molecules of reactants react and form a single product molecule having three ester groups and three water molecules. As the starting reactants contain two functional groups in its molecule, the resultant product molecule is still capable of reacting further to form a bigger molecule.



$$\underset{\text{Ethylene glycol}}{CH_2OH-CH_2OH} + \underset{\text{Adipic acid}}{HOOC-(CH_2)_4-COOH} \longrightarrow H_2O + \underset{\text{Monoester product}}{HOCH_2CH_2OOC-(CH_2)_4COOH}$$

$$\underset{\text{Adipic acid}}{HOOC-(CH_2)_4-COOH} + \underset{\text{Monoester product}}{HOCH_2CH_2OOC-(CH_2)_4COOH} + \underset{\text{Ethylene glycol}}{CH_2OH-CH_2OH} \longrightarrow$$

$$HOOC-(CH_2)_4-COOCH_2-CH_2OOC-(CH_2)_4-COOCH_2-CH_2OH + 2H_2O$$

The overall reaction can also be written as :

$$\underset{\substack{\text{Ethylene glycol}\\ \text{(2 molecules)}}}{2HOCH_2-CH_2OH} + \underset{\substack{\text{Adipic acid}\\ \text{(2 molecules)}}}{2HOOC-(CH_2)_4-COOH} \longrightarrow$$

$$HO-[CH_2-CH_2COO-(CH_2)_4COO]_7-H + 3H_2O$$

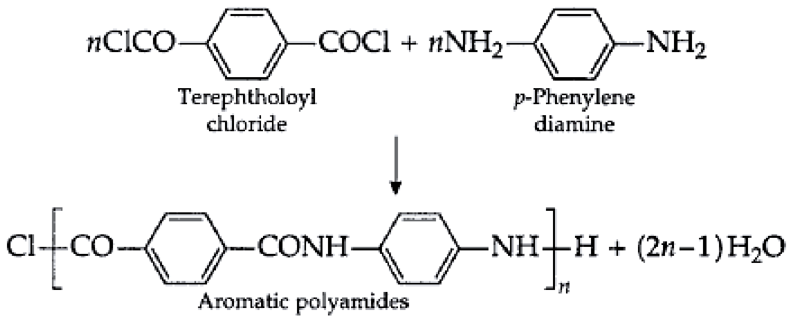
2. INTERFACIAL CONDENSATION POLYMERISATION

In this type of polymerisation, two different medium are taken and product is formed at the point of interface between two phases. Here, one phase is an aqueous solvent and another phase is an organic medium. In such technique, the reactants contain highly reactive functional groups which can react readily at ambient temperatures and produce condensation products.

In an actual process of production, the two solutions are thoroughly agitated, and thus formation of an emulsion takes place. In the same time, the interface surface/volume ratio is increased and, hence, both the rate and degree of polymerisation becomes too high. As the product is produced, it forms slurry due to high-speed agitation. The formed polymer precipitates out, isolated from the slurry and washed well.

In a typical example of interfacial condensation, *p*-phenylene diamine is dissolved in water and terephtholoyl chloride is taken in chloroform or carbon tetrachloride. When these two solutions are brought in contact with each other, the diamine molecules diffuse into the organic phase and react with acid chloride at the interface. Meanwhile, the polymer is formed, which is precipitated out immediately. In this process a by product, HCl, is generated which diffuses back into the aqueous phase. When the polymer is isolated from the interface, a fresh surface of the acid chloride molecules in the organic phase is exposed, which form again a thin film of new polymer molecules at the interface.

Since the formation of polymer at the interface is a diffusion-controlled process, a very high molecular weight polymer can be obtained by this technique. The process of polymerisation is expressed as:



3. POLYMERISATION IN HOMOGENEOUS 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.

(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 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.

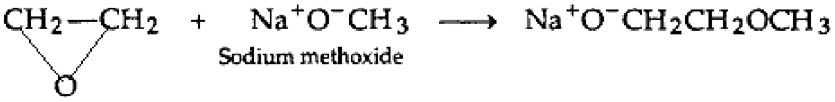
The polymer formed is in molten state at the reaction temperature and it is important to isolate it from the reactor during hot condition, otherwise it will solidify inside the reactor and removal becomes very hard.

4. RING-OPENING POLYMERISATION

In this polyrnerisation, monomers containing a ring structure can be opened and polyrnerised under certain favourable conditions. The cyclic compounds such as oxiranes and lactams can be opened up in presence of aqueous alkali or acids, and form an intermediate. This intermediate product contains active end groups which can undergo polymerisation reaction. The ring-opening polymerisation can be involved in the monomers of ethylene oxide (an heterocyclic oxirane ring compound) and sodium methoxide (dissolved in dioxane).

In the ***initiation*** step, sodium methoxide molecule attacks on oxirane ring and cleaves it into anion

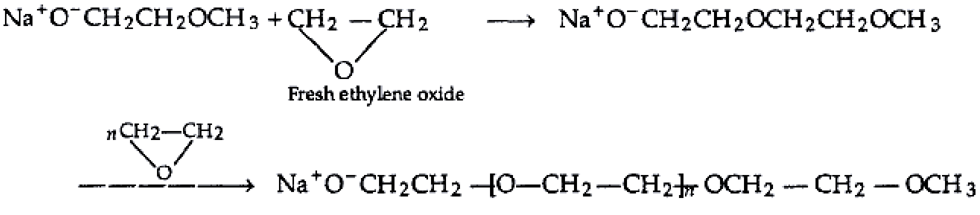
Initiation



Ethylene glycol

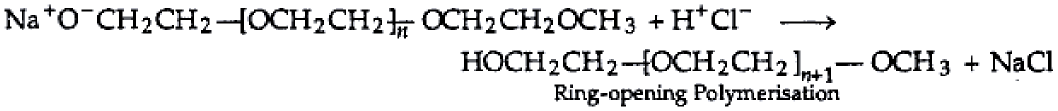
Propagation starts: This step is brought about by the anion attacking a fresh ethylene oxide ring which will be opened up and added on with the simultaneous formation of an anion, thus this process goes on.

Propagation



In the ***termination*** step started, where HCI is added. HCI donates a proton to the anion molecule as follows:

Termination



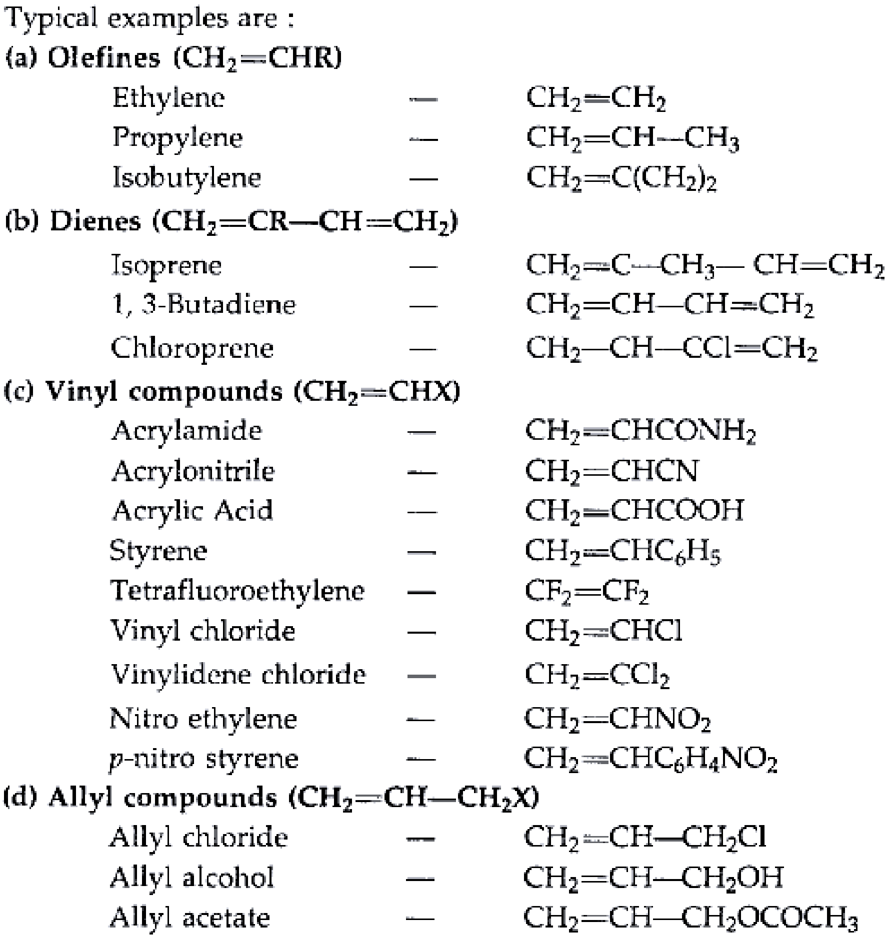
$$Na^+O^-CH_2CH_2-[OCH_2CH_2]_n-OCH_2CH_2OCH_3 + H^+Cl^- \longrightarrow HOCH_2CH_2-[OCH_2CH_2]_{n+1}-OCH_3 + NaCl$$

Ring-opening Polymerisation

Since ring-opening polymerisation is similar to anion chain (addition) polymerisation, even then there is a minor difference. In ring-opening, the attack by the anion is on the activated ring, while in anion-chain polymerisation, it is on the 7t electron pair of the C=C bond.

5. ADDITION (CHAIN) POLYMERISATION

This type of polymerisation is characterised by a self-addition of the monomer molecules, rapidly through a chain reaction. The product has the same composition as that of the monomer molecules. In this reaction no byproduct is formed. Since them compounds containing reactive double bonds, therefore, can proceed by a chain reaction mechanism.



Typical examples are :

(a) Olefines ($CH_2=CHR$)

Ethylene — $CH_2=CH_2$
Propylene — $CH_2=CH-CH_3$
Isobutylene — $CH_2=C(CH_2)_2$

(b) Dienes ($CH_2=CR-CH=CH_2$)

Isoprene — $CH_2=C-CH_3-CH=CH_2$
1, 3-Butadiene — $CH_2=CH-CH=CH_2$
Chloroprene — $CH_2-CH-CCl=CH_2$

(c) Vinyl compounds ($CH_2=CHX$)

Acrylamide — $CH_2=CHCONH_2$
Acrylonitrile — $CH_2=CHCN$
Acrylic Acid — $CH_2=CHCOOH$
Styrene — $CH_2=CHC_6H_5$
Tetrafluoroethylene — $CF_2=CF_2$
Vinyl chloride — $CH_2=CHCl$
Vinylidene chloride — $CH_2=CCl_2$
Nitro ethylene — $CH_2=CHNO_2$
p-nitro styrene — $CH_2=CHC_6H_4NO_2$

(d) Allyl compounds ($CH_2=CH-CH_2X$)

Allyl chloride — $CH_2=CH-CH_2Cl$
Allyl alcohol — $CH_2=CH-CH_2OH$
Allyl acetate — $CH_2=CH-CH_2OCOCH_3$

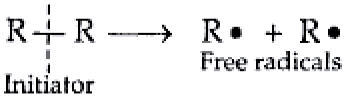
Addition polymerisation reactions consist of three important steps: (i) initiation (ii) propagation and (iii) termination. The entire process can be brought about by a ***free radical***, ***ionic (carbonium ion or carbanion)*** or ***coordination*** mechanism. Depending on the mechanism, we will discuss here three types of addition chain polymerisation:

1. Free-Radical Addition Polymerisation

The polymer chain is initiated by free radicals produced by the decomposition of compounds called initiators:

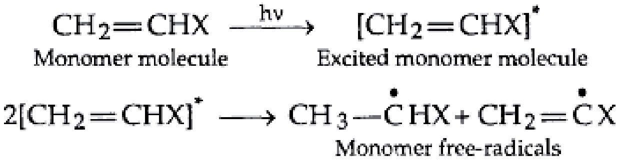
Initiators: The initiators are thermally unstable compounds. When energy is supplied, they decompose into two identical fragments by 'homolytic decomposition'. Each fragment carries one unpaired (lone) electron with it; and called free radicals.

If R-R is an initiator, it may split into two symmetrical components at its bond between the two R-R as:



$$\underset{\text{Initiator}}{R\text{—}R} \longrightarrow \underset{\text{Free radicals}}{R\bullet + R\bullet}$$

The low molecular weight compounds mainly azo, peracids, peroxides, peresters, hydroperoxides are useful as initiators. Initiators can be decomposed and form free radicals whiie induced by heat energy, light energy or catalysts. The initiators can also be decomposed by using ultraviolet light and form the same free radicals as those formed by its thermal decomposition. Free-radicals can be also produced by direct excitation of the monomer molecules in UV light as:



$$\underset{\text{Monomer molecule}}{CH_2{=}CHX} \xrightarrow{h\nu} \underset{\text{Excited monomer molecule}}{[CH_2{=}CHX]^*}$$

$$2[CH_2{=}CHX]^* \longrightarrow \underset{\text{Monomer free-radicals}}{CH_3\text{—}\dot{C}HX + CH_2{=}\dot{C}X}$$

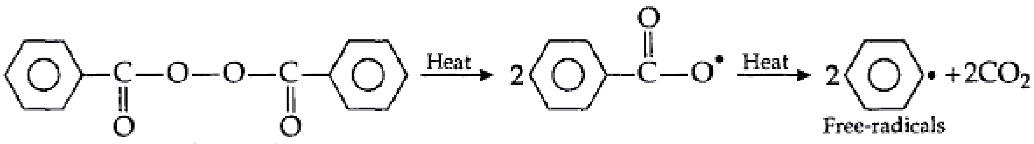
The polymerisation reactions initiated by UV light are known as 'photoinitiated polymerisation'.

Free-radicals are also formed when initiators are induced by suitable catalysts. The decomposition of hydrogen peroxide by a ferrous ion and hydroperoxide by a cobaltous ion are the examples of initiators, decomposed by reduction-oxidation (redox) reaction. Polymerisation reactions using these redox initiators are termed as 'redox polymerisation', as shown below:

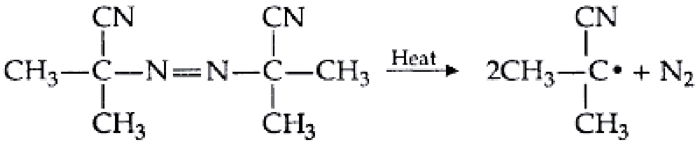
$$\underset{\text{Hydrogen peroxide}}{H_2O_2} + Fe^{2+} \longrightarrow HO^- + HO^\bullet + Fe^{3+}$$

$$\underset{\text{Hydroperoxide}}{R\text{—}O\text{—}OH} + Co^{2+} \longrightarrow R\dot{O} + HO^- + Co^{3+}$$

$$R\text{—}O\text{—}OH + Co^{3+} \longrightarrow RO\dot{O} + H^+ + Co^{2+}$$



Benzoyl peroxide



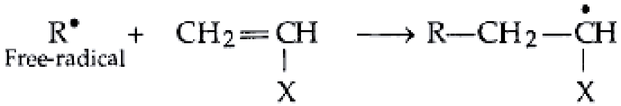
$$CH_3\text{—}\underset{CH_3}{\overset{CN}{C}}\text{—}N{=}N\text{—}\underset{CH_3}{\overset{CN}{C}}\text{—}CH_3 \xrightarrow{\text{Heat}} 2CH_3\text{—}\underset{CH_3}{\overset{CN}{C}}\bullet + N_2$$

Azo bis isobutyro nitrile Free radicals

The initiators decomposed into free-radicals by thermal energy can be illustrated by the following examples:

The rate of decomposition of these initiators depends on the reaction temperature, solvents used, and the intensity and wavelength of the radiations.

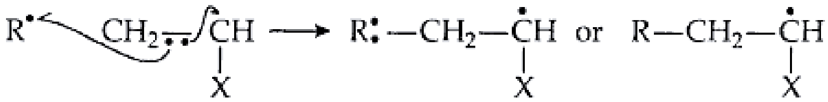
Initiation: A free-radical contains an unpaired electron; which always search a lone electron to couple with and get stabilised itself. Free-radical is, therefore, highly reactive species which attacks the double bond in the monomer molecule in such a manner:



$$\underset{\text{Free-radical}}{R^\bullet} + CH_2{=}\underset{X}{CH} \longrightarrow R\text{—}CH_2\text{—}\underset{X}{\dot{C}H}$$

Monomer Molecule

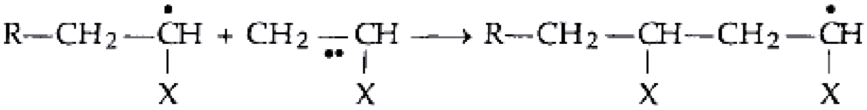
A double bond formed between two carbon atoms, C=C, one pair of electrons is called (σ-) sigma electrons, while the other pair exists as (π) electrons. The n electrons are not very dose to nucleus; therefore, they are susceptible to attack by other reactive species. By the homolytic decomposition of the initiator free-radicals are produced, which combine with one of the π electrons and forms a normal pair of electrons at the sigma level, and the other electron of the π pair is transferred to the other end of the molecule as given below:



$$R^\bullet\ CH_2{:}\underset{X}{CH} \longrightarrow R{:}\text{—}CH_2\text{—}\underset{X}{\dot{C}H} \text{ or } R\text{—}CH_2\text{—}\underset{X}{\dot{C}H}$$

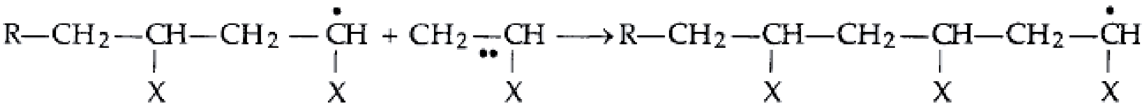
Now, the monomer unit is linked to the free-radical unit through a sigma bond forming a single molecule. The other electron of the original n electron pair becomes unpaired and deprived of a new partner. Thus, this whole sequence, in which one free-radical attacks a monomer molecule and adds with it, simultaneously transfers the free-radical site from itself to the monomer unit is called the ***initiation step***.

Propagation: After initiation step, the propagation step gets started, where the free-radical site at the first monomer unit attacks the double bond of a fresh monomer unit. Thus, the second monomer molecule links with the first and the transfer of the radical site from the first monomer molecule to the second takes place by the unpaired electron transfer process as shown below:



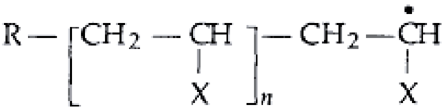
$$R-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + CH_2 \underset{\bullet\bullet}{=} \underset{X}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

This chain again contains a radical site at its end carbon atom and can attack another monomer molecule with a transfer of the radical site to the new monomer molecule as follows:



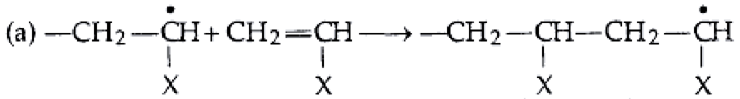
$$R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + CH_2 \underset{\bullet\bullet}{=} \underset{X}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

This process continuing attack on new monomer molecules and adding to the growing chain to the one after another. The whole process lasts till the chain growth is stopped due to absence of further fresh monomer left for attack or if the free-radical site is killed by some impurities. The entire process is called ***propagation*** which can be shown as:



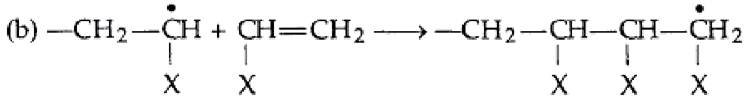
$$R-\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_n-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

where n denotes the monomer molecules added in the chain growth. In the growing chain, the mode of the addition of monomer molecule can be of the head-to-tail, head-to-head, tail-to-head or tail-to-tail type. Suppose, the -CH_2- is the head and -CHX- is tail part of a monomer unit, the four types of propagation can be shown as:



$$\text{(a)}\ -CH_2-\underset{X}{\underset{|}{\dot{C}H}} + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow -CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

Head-to-tail addition

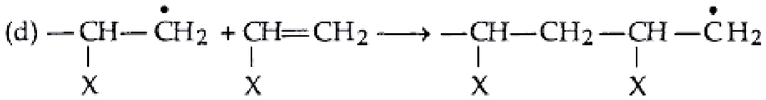


$$\text{(b)}\ -CH_2-\underset{X}{\underset{|}{\dot{C}H}} + \underset{X}{\underset{|}{CH}}=CH_2 \longrightarrow -CH_2-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{\dot{C}H_2}}$$

Tail-to-tail addition

$$\text{(c)}\ -\underset{X}{\underset{|}{CH}}-\dot{C}H_2 + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow -\underset{X}{\underset{|}{CH}}-CH_2-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

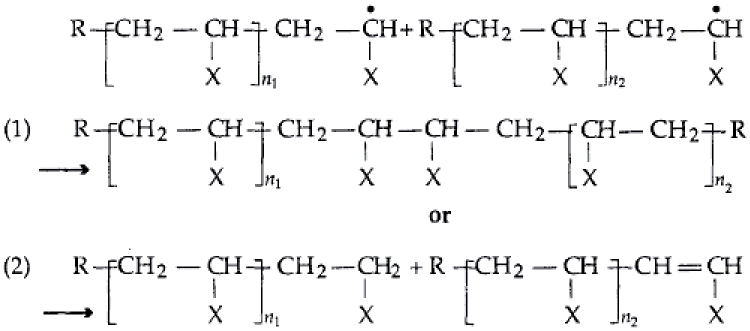
Head-to-head addition



$$\text{(d)}\ -\underset{X}{\underset{|}{CH}}-\dot{C}H_2 + \underset{X}{\underset{|}{CH}}=CH_2 \longrightarrow -\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-\dot{C}H_2$$

Tail-to-head addition

Termination: The termination process starts after the propagation when further addition of the monomer molecule to the chain is stopped. Termination is the removal of the active centre of a polymer. On the basis of time, temperature, monomer unit and initiator concentration, a statistical probability of the two growing chains is occurred (present in the system) which come close and collide each other. When this collision takes place, the following two reactions occur which resulted in the arrest of the chain growth:



$$R-\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{\dot{C}H}+R-\left[CH_2-\underset{X}{CH}\right]_{n_2}CH_2-\underset{X}{\dot{C}H}$$

$$(1)\quad \longrightarrow R-\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2-\left[\underset{X}{CH}-CH_2\right]_{n_2}-R$$

or

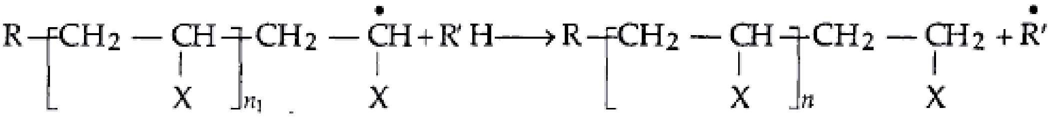
$$(2)\quad \longrightarrow R-\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{CH_2}+R-\left[CH_2-\underset{X}{CH}\right]_{n_2}CH=\underset{X}{CH}$$

In above reactions (I), it shows that the two chains combine by the coupling of unpaired electrons and form a sigma bond. Such type of termination is called 'termination by coupling' because this process involves the coupling of the one lone pair of electrons.

In the reaction (2), one H-atom from one chain is abstracted by the other chain, and utilised unpaired electron, whereas the chain which has donated the H-atom, gets stabilised and form a double bond. In this reaction, two polymer molecules are formed. Both the molecules consist of shorter chain length as against a single molecule of a longer chain length. Such type of termination is known as ***'termination by disproportionation**.'*

Thus, in above cases, the product molecule is formed known as polymer. This product does not consist of any free-radical site and, hence, cannot grow any further. The process of termination thus causes in deactivation of growing chain. The groups which are present at the end of the chain are called the 'end groups'. For example, in above cases, these groups are -R, and -CH_2=CHX.

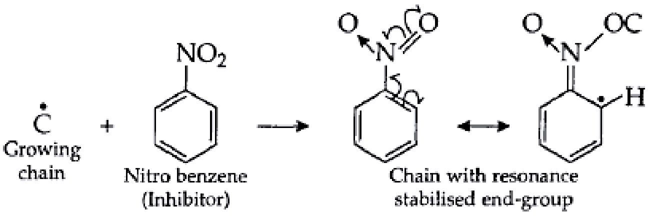
Chain Transfer: There is another method of chain termination, which takes place by the 'transfer reaction'. In this reaction, the growth of one polymer chain is deactivated and gets stopped, meanwhile, there is a generation of a new free-radical which starts a new polymer chain growth. The transfer reaction occurs by the abstraction of a H-atom or some other atom present in the system. This process follows as:



$$R-\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\underset{X}{\dot{C}H}+R'H\longrightarrow R-\left[CH_2-\underset{X}{CH}\right]_{n}CH_2-\underset{X}{CH_2}+\dot{R}'$$

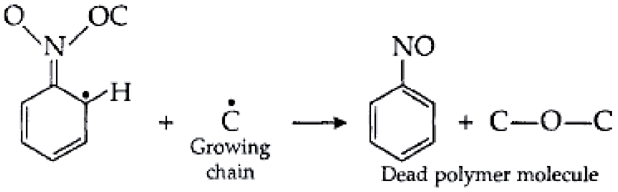
Now, a new free-radical R$^\cdot$ is generated and the growing chain gets terminated. Thus, R$^\cdot$ is ready to initiate as well as propagate a fresh chain growth. Here, the termination of one chain growth and the initiation of a new one takes place simultaneously. Since the chain growth is transferred from one site to another, the process is known as '**chain transfer**'.

Inhibitors: In the polymer industry, several inhibitors are used which are capable of inhibiting or killing the chain growth by uniting with the active free-radicals and producing inactive free-radicals. A few examples of these inhibitors are nitrobenzene, hydroquinone, benzothiazine, dinitrobenzene, etc. The inhibiting action of these chemical substances can be represented as:



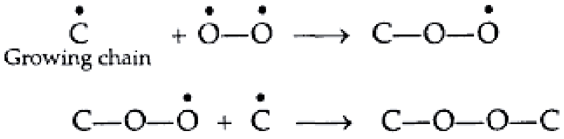
In this reaction the inhibitor (nitrobenzene) adds on the growing chain C and forms a polymer chain with nitrobenzene resonance stability end group and carrying a radical site.

The free-radical nature of the end group is strong enough to reunite with the radical of another growing chain and terminate the growth of it as follows:



In this case, it is observed that a single inhibitor molecule has killed two growing chains.

The atmospheric oxygen is a good inhibitor; therefore, the free-radical polymerisation is generally carried out under an atmosphere of nitrogen. Due to the biradical nature of oxygen atom, the inhibiting action takes place in a powerful way as represented below:



$$\underset{\text{Growing chain}}{\dot{\mathrm{C}}} + \dot{\mathrm{O}}\text{—}\dot{\mathrm{O}} \longrightarrow \mathrm{C}\text{—}\mathrm{O}\text{—}\dot{\mathrm{O}}$$

$$\mathrm{C}\text{—}\mathrm{O}\text{—}\dot{\mathrm{O}} + \dot{\mathrm{C}} \longrightarrow \mathrm{C}\text{—}\mathrm{O}\text{—}\mathrm{O}\text{—}\mathrm{C}$$

2. Ionic Polymerisation

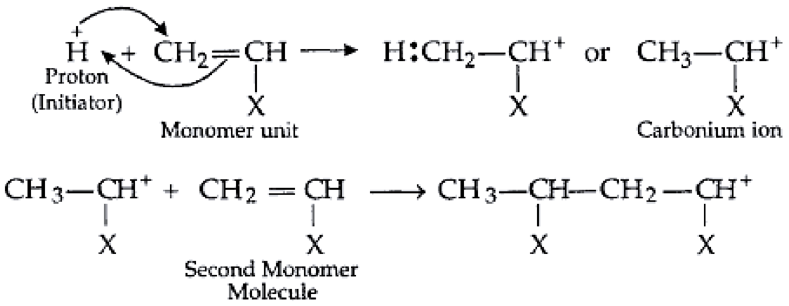
The ionic polymerisation is divided into two categories:

(i) Cationic polymerisation

(ii) Anionic polymerisation

(i) Cationic Polymerisation: In this type of polymerisation, initiators and monomers are used during the chain growth; however, the initiation is done by a proton and the propagation carried out by a carbonium ion. In cationic polymerisation, the initiators used are strong Lewis acids such as BF_3, $SnCl_4$, $TiCl_4$, $AlCl_3$ and are called '*catalysts*'. The monomers, which can undergo for this purpose are styrene, methyl styrene, many vinyl ethers and isobutylene.

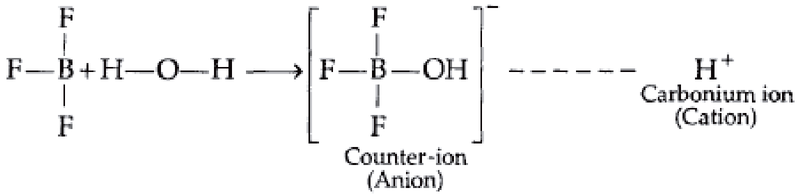
The mechanism of this polymerisation involves an attack on the 1t electron pair of the monomer molecule. In the chain reaction, first a proton is introduced into a monomer. The proton attracts the π electron pair towards it and a positive charge of the proton is transferred to the end of the monomer molecule; thus forms a carbonium ion. In this reaction, a sigma bond is formed between the proton and monomer molecule and the polymer chain growth started. This is an '**initiation**' process; where the carbonium ion attacks on the π electron pair of the second monomer molecule and attracts it over. The positive charge is transferred to the far end of the second monomer molecule. Thus a chain reaction begins, where only a displacement of the electron pair and the formation of a carbonium ion takes place. The whole process can be represented in the following manner:



$$\overset{+}{H} + CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow H{:}CH_2{-}\underset{X}{\underset{|}{CH^+}} \text{ or } CH_3{-}\underset{X}{\underset{|}{CH^+}}$$

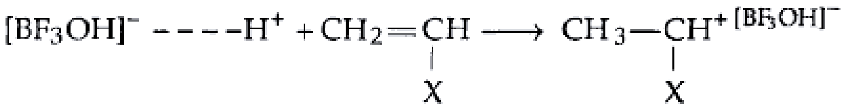
$$CH_3{-}\underset{X}{\underset{|}{CH^+}} + CH_2 = \underset{X}{\underset{|}{CH}} \longrightarrow CH_3{-}\underset{X}{\underset{|}{CH}}{-}CH_2{-}\underset{X}{\underset{|}{CH^+}}$$

The above process occurs in the presence of a 'catalyst' (e.g., BF_3) and a 'co-catalyst' (e.g., water or methanol), and form hydrates as follows:



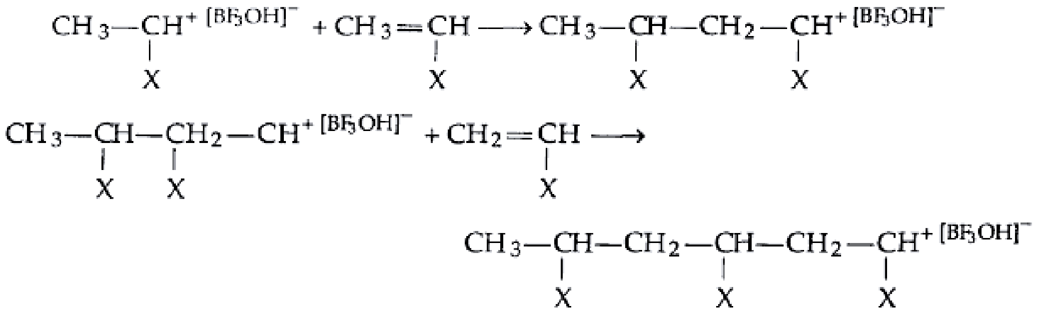
$$F{-}\underset{F}{\underset{|}{\overset{\overset{F}{|}}{B}}} + H{-}O{-}H \longrightarrow \left[F{-}\underset{F}{\underset{|}{\overset{\overset{F}{|}}{B}}}{-}OH\right]^{-} \text{------} \; H^+$$

Now the H^+ ion attacks the π electron pair of the second monomer molecule, and initiates the chain growth through the carbonium ion and the $[BF_3OH]^-$ anion as follows:



$$[BF_3OH]^- \text{----} H^+ + CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow CH_3{-}\underset{X}{\underset{|}{CH}}{}^{+\,[BF_3OH]^-}$$

In propagation step, addition of further monomer unit and transfer of the charge to the newly added monomer molecule takes place which as shown below:



$$CH_3-\underset{X}{CH}^+[BF_3OH]^- + CH_3=\underset{X}{CH} \longrightarrow CH_3-\underset{X}{CH}-CH_2-\underset{X}{CH}^+[BF_3OH]^-$$

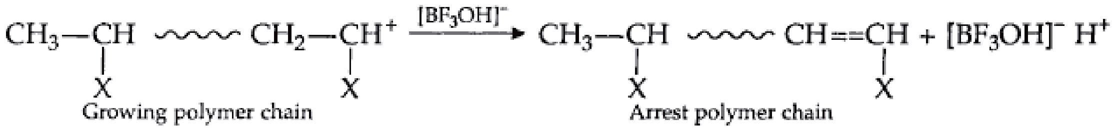
$$CH_3-\underset{X}{CH}-\underset{X}{CH_2}-CH^+[BF_3OH]^- + CH_2=\underset{X}{CH} \longrightarrow$$

$$CH_3-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}^+[BF_3OH]^-$$

Since, the addition of monomer units are increased, the chain keeps on growing, the π electron pairs of the monomer molecules are pulled in opposite direction to the growth of the chain.

After propagation process, termination starts when a collision between carbonium ion and an anion takes place. Termination occurs by following two steps:

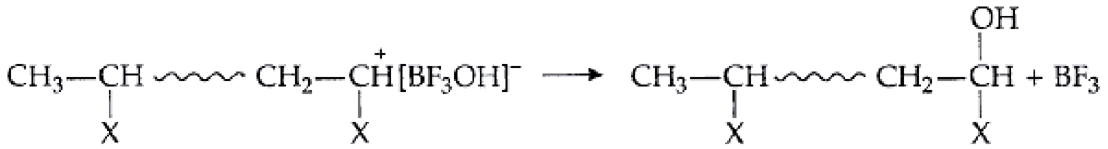
(a) The termination process causes the arrest of the chain growth, where donation of a proton to the counter-ion resulting in the formation of a double bond at the end of the growing polymer molecule:



$$CH_3-\underset{X}{CH} \sim\sim\sim CH_2-\underset{X}{CH}^+ \xrightarrow{[BF_3OH]^-} CH_3-\underset{X}{CH} \sim\sim\sim CH{=}{=}\underset{X}{CH} + [BF_3OH]^- H^+$$

In this process, a proton is donated and BF_3 hydrate is re-formed. It is called '***ion-pair precipitation***'.

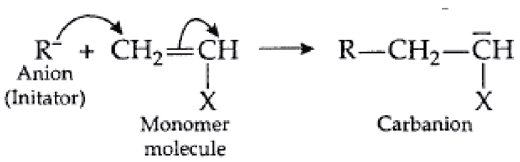
(b) In this process, termination occurs by simple '***coupling***', when a covalent bond is formed between carbonium ion (C^+) and the counter-ion. It is represented as follows:



$$CH_3-\underset{X}{CH} \sim\sim\sim CH_2-\underset{X}{\overset{+}{CH}}[BF_3OH]^- \longrightarrow CH_3-\underset{X}{CH} \sim\sim\sim CH_2-\underset{X}{\overset{OH}{CH}} + BF_3$$

(ii) Anionic Polymerisation: In anionic polymerisation, a negatively charged ion attacks on 1t electron pair of the monomer molecule and pushing it as far away as possible, i.e., to the end of the molecule. Simultaneously, it forms a sigma bond with the monomer unit.

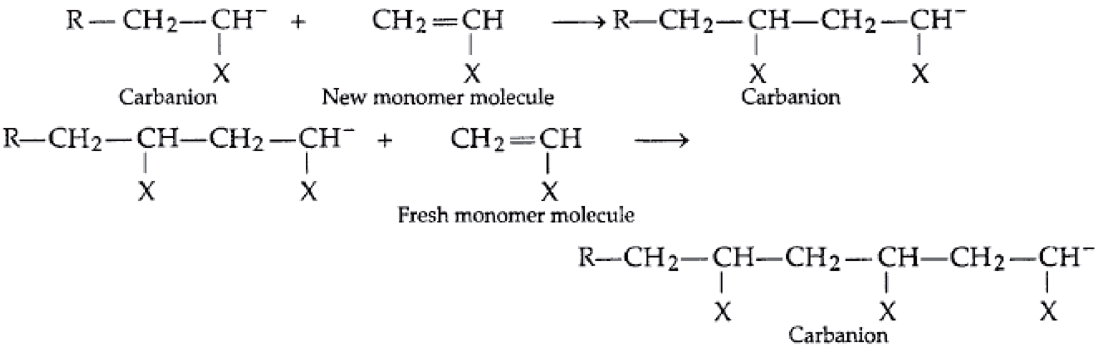
At the same time, a carbanion is also formed. This is represented as follows:



Now the propagation process starts. It is initiated by newly formed carbanion, which attacks on the second monomer unit. Thus the 1t electron pair pushed away to the end of the molecule. Again a new sigma bond is formed between the carbanion and monomer unit. In this electron pair displacement process, the negatively charged ion pushes the 1t electron pair of the monomer double bond down to sigma electron level.

In termination process, some strong ionic substances are added deliberately. In ionic polymerisation, termination is not usually a spontaneous process. If some substances are not added, the reaction proceeds till the entire monomer molecule is consumed. Thus, if there is no more monomer is left for polymerisation, the carbanions at the chain ends remain active which may initiate the polymerisation when a fresh monomer is added. Studies have shown that by adding a fresh quantity of monomers, the anionic polymerisation can be restarted, even after weeks. The polymers formed by this manner are called ***'living polymers'*** and such technique is known as ***'living polymerisation technique'***. Example of this type of polymer is 'block copolymer.

The anionic polymerisation is represented as:



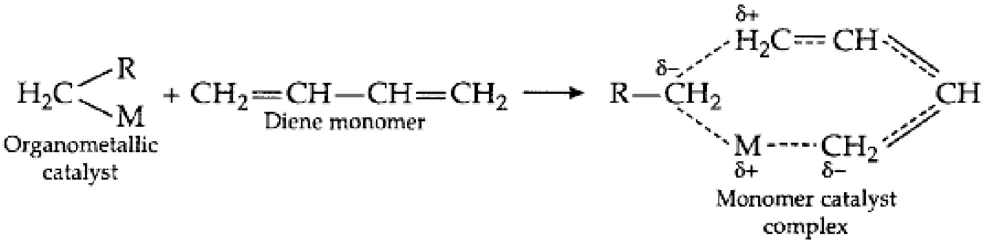
In this case the initiators used are generally the organo-alkali compounds such as ethyl sodium, butyl lithium, triphenyl methyl potassium. Similarly, alkali metal amides, hydroxides and alkoxides can also be used for the anionic polymerisation process.

The monomer molecules, which are used to undergo anionic polymerisation, include styrene, butadiene, acrylonitrile and isoprene.

The fundamental difference between cationic and anionic polymerisation is that cationic process consists of the movement of the π electron pair in a opposite direction to that of the chain growth, while in latter case, it is in the same direction as that of the chain growth.

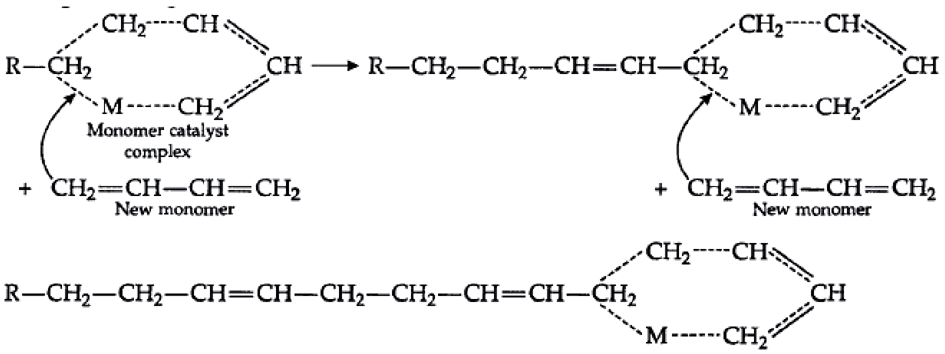
3. Coordination Polymerisation (Polyenes)

In coordination polymerisation reactions the monomer molecules used are generally ***dienes*** and ***olefines***. These reactions are catalysed by organo-metallic compounds. In such polymerisation, a ***monomer-catalyst complex*** is formed between the monomer and organometallic compound. A coordination bond is used between a carbon atom of the monomer and the metal atom of the catalyst, thus formation of monomer-catalyst complex takes place. The polymerisation process proceeds as follows:

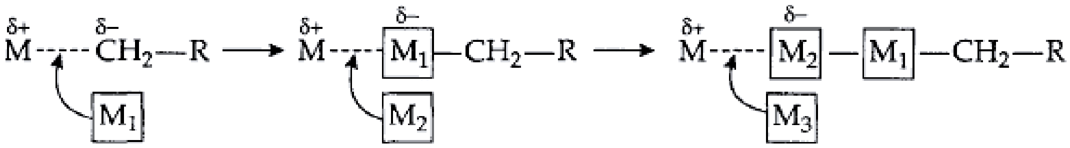


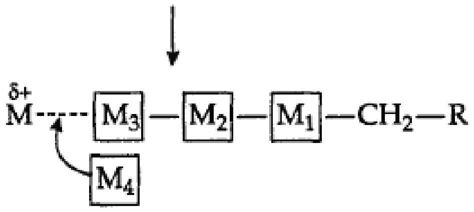
where, M = Transition metals such as Ni, Cr, Mo, V, Ti or Rh.

A coordinated metal-carbon bond is formed in the monomer-catalyst complex. This is known as the active centre. The propagation process starts at the active centre site where the chain growth begins as:



Coordination polymerisation is also known as '**insertion polymerisation**', because the monomer molecule is inserted in between the metal ion and carbanion.

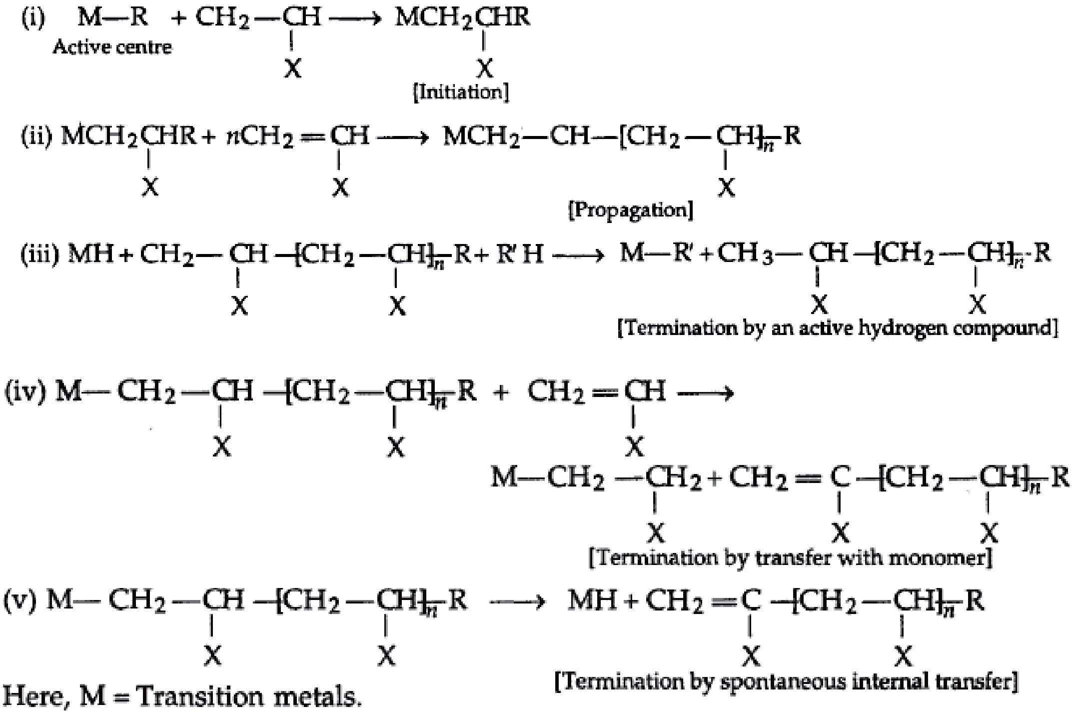




Here, M=metal ion, and M_1, M_2, M_3, M_4, etc., are the first, second, third and fourth monomer units which are added to the polymer growing chain.

In this polymerisation, the metal counter-ion is placed in a specific special arrangement with respect to the anion. In some catalyst systems, the spatial arrangement has a large effect on spatial orientation of the incoming monomer and also on the manner in which the monomer is inserted into the growing chain and this imparts stereo-regularity to the polymer formed. A highly stereo-regular polymer can be formed by using a proper catalyst (e.g., Ziegler-Natta catalyst) and solvent system.

Thus, the coordination polymerisation is characterised by the initiation, propagation and termination reactions as given below:



(i) $\underset{\text{Active centre}}{M-R} + CH_2-\underset{X}{CH} \longrightarrow MCH_2\underset{X}{C}HR$

[Initiation]

(ii) $MCH_2\underset{X}{C}HR + nCH_2=\underset{X}{CH} \longrightarrow MCH_2-CH-[CH_2-\underset{X}{CH}]_n R$

[Propagation]

(iii) $MH + CH_2-\underset{X}{CH}-[CH_2-\underset{X}{CH}]_n R + R'H \longrightarrow M-R' + CH_3-\underset{X}{CH}-[CH_2-\underset{X}{CH}]_n \cdot R$

[Termination by an active hydrogen compound]

(iv) $M-CH_2-\underset{X}{CH}-[CH_2-\underset{X}{CH}]_n R + CH_2=\underset{X}{CH} \longrightarrow M-CH_2-\underset{X}{C}H_2 + CH_2=\underset{X}{C}-[CH_2-\underset{X}{CH}]_n R$

[Termination by transfer with monomer]

(v) $M-CH_2-\underset{X}{CH}-[CH_2-\underset{X}{CH}]_n R \longrightarrow MH + CH_2=\underset{X}{C}-[CH_2-\underset{X}{CH}]_n R$

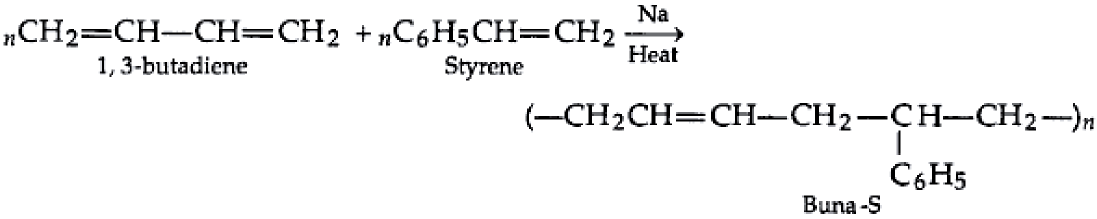
[Termination by spontaneous internal transfer]

Here, M = Transition metals.

6. COPOLYMERISATION

When a single monomer or a single monomer pair is polymerised and form a polymer, the process is called '***homopolymerisation***'.

On the other hand, two or more monomers or monomer pairs are polymerised simultaneously; the polymer is composed of more than one repeat unit, hence termed as '***copolymerisation***'. The example of such reaction is styrene-butadiene rubber (SBR), the first synthetic made rubber, and is a copolymer of I, 3-butadiene and styrene which can be, formed in the ratio of 3 : 1 in the presence of sodium as:



$$\underset{\text{1, 3-butadiene}}{{}_nCH_2{=}CH{-}CH{=}CH_2} + \underset{\text{Styrene}}{{}_nC_6H_5CH{=}CH_2} \xrightarrow[\text{Heat}]{\text{Na}} \underset{\text{Buna -S}}{(-CH_2CH{=}CH{-}CH_2{-}\underset{\displaystyle C_6H_5}{\underset{|}{C}}H{-}CH_2{-})_n}$$

In Buna-S, Bu stands for butadiene; Na for sodium and 5 stands for styrene. This co polymer is obtained by the free-radical polymerisation and composed of both butadiene as well as styrene repeat units.

The copolymerisation can be discussed under following types of polymerisation reactions:

(a) Free-Radical Copolymerisation (and its kinetics)

In the free-radical copolymerisation reaction, free-radical initiator, R, is used with monomers M_1 and M_2 and mixed well for polymerisation. The free-radical $R^{\cdot}$ attacks on M_1 and M_2. This is an initiation step as:

$$R^{\bullet} + M_1 \longrightarrow RM_1^{\bullet}$$
$$R^{\bullet} + M_2 \longrightarrow RM_2^{\bullet}$$

In the propagation step, the above chain can further attack on M_1 or M_2.

$$R\dot{M}_1 + M_1 \longrightarrow RM_1\dot{M}_1$$
$$R\dot{M}_1 + M_2 \longrightarrow RM_1\dot{M}_2$$
$$R\dot{M}_2 + M_1 \longrightarrow RM_2\dot{M}_1$$
$$R\dot{M}_2 + M_2 \longrightarrow RM_2\dot{M}_2$$

To predict the composition of the copolymer, we must establish a suitable kinetic scheme. In 1936, ***Dostal*** proposed following group of homo and hetero-polymerisation reactions for a radical copolymerisation between two monomers, M_1 and M_2, and ultimately established a practical equation from the reactions:

$$\dot{M}_1 + M_1 \xrightarrow{k_{11}} M_1\dot{M}_1$$
$$\dot{M}_1 + M_2 \xrightarrow{k_{12}} M_1\dot{M}_2$$
$$\dot{M}_2 + M_1 \xrightarrow{k_{21}} M_2\dot{M}_1$$
$$\dot{M}_2 + M_2 \xrightarrow{k_{22}} M_2\dot{M}_2$$

where K_{II} and K_{22} are the rate constants for the ***self-propagating*** reactions and K_{I2} and K_{21} are the corresponding ***cross-propagation*** rate constants. Now, the rates of these four propagation reactions are as follows:

$$R_{11} = K_{11}\ [\dot{M}_1][M_1]$$
$$R_{12} = K_{12}\ [\dot{M}_1][M_2]$$
$$R_{21} = K_{21}\ [\dot{M}_2][M_1]$$
$$R_{22} = K_{22}\ [\dot{M}_2][M_2]$$

Under steady-state conditions, and assuming that the radical reactivity is independent of chain length and depends only on the nature of the terminal unit, the rate of the consumption of M_1 from the initial reaction mixture is then:

$$-d[M_1] / dt = K_{11}\ [M_1][\dot{M}_1] + K_{21}\ [M_1][\dot{M}_2] \qquad \dots(1)$$

and M_2 by,
$$-d[M_2] / dt = K_{22}\ [M_2][\dot{M}_2] + K_{12}\ [M_2][\dot{M}_1] \qquad \dots(2)$$

The copolymer equation can then be obtained by dividing equation (1) by (2) and\ assuming that

$K_{21} = [\dot{M}_2][M_1] = K_{12}\ [\dot{M}_1][M_2]$ for steady-state conditions, so that—

$$d[M_1] / d[M_2] = ([M_1] / [M_2])\{r_1\ [M_1] + [M_2] / ([M_1] + r_2[M_2])\}$$

where $K_{11} / K_{12} = r_1$, and $K_{22} / K_{21} = r_2$

The quantities r_1 and r_2 are the relative reactivity ratios defined as the "ratio of the reactivity of the propagating species with its own monomer to the reactivity of the propagating species with the other monomer".

Monomer Reactivity Ratios: In a given reaction mixture, the amount of each monomer of the chain can be calculated by the copolymer equation. This equation suggests that if the monomer M_1 is more reactive than M_2, the M_1 will enter in the copolymer more quickly. The equation is then an expression which relates to the reaction mixture composition at any given time.

If the copolymerisation is to be completely understood, it is necessary to obtain a reliable values of r for each pair of monomers. By analysing the composition of the copolymer from a number of monomer (comonomer) mixtures with various $[M_1] / [M_2]$ ratios, the values of r can be achieved.

If F_I and F_2 are mole fractions of monomers M_1 and M_2 being added to the growing chain, and f_1 and f_2 are the corresponding mole fractions of the monomers in the reaction mixture, then the copolymer equation can be written as:

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2) \qquad \ldots(a)$$

and, if $F = (F_1/F_2)$ and $f = (f_1/f_2)$ ...(b)

To give $[f(1 - F) / F] = r_2 - (f^2 / F) r_1$

which is a linear form of equation (a), and was given by *Finemann* and *Ross*. A plot between [f (1- F)/F and (f^2/F) then must be linear and yield r_1 from the slope and r_2 from intercept.

Reactivity Ratios and Copolymerisation Behaviour:

As we know that the terms:

$r_1 = K_{11}/K_{12}$

$r_2 = K_{22}/K_{21}$

when $r_1 = 1$, the propagation rate constants are the same for the reaction type 11 and 12, and consequently a growing chain containing radical end MI can add either the monomer molecules M_1 or M_2 with equal probability.

When $r_1 < 1$, then the M_2 monomer will be added in chain more rapidly than M_1

When $r_1 > 1$, then the M_1 monomer will be added more readily than M_2. The same will be happened for r_2 also.

Now, on the basis of the r_1 and r_2 values, different types of copolymerisation behaviours are discussed below:

(1) When $r_1 = r_2 = 0$

In this case, the propagation reaction types 11 and 22 are not possible, hence, a chain ending with M_1 will add only on M_2 and this M_2 will add only on M_1, which will add only on M_2 and so on. In other words, the copolymer formed will have an equal number of M_1 and M_2 monomeric units arranged alternatively in the copolymer chain and formed an alternating copolymer.

(2) When $r_1 = r_2 = 1$

In this case, all the propagation types (11, 12, 21, 22) reactions are equally possible. A growing chain ending with M_1 can add either M_1 or M_2 and, a chain ending with M2 can add either M_1 or M_2. The probability of M_1 and M_2 adding to the M_1 or M_2 depends on the concentrations of monomer. This type of copolymerisation is called an ***'ideal copolymerisation'*** or ***'azeotropic copolymerisation'*** because the copolymer thus formed will have the same ratio of the monomeric units as that of the monomer reaction mixture. The two monomer units arranged in the chain remain in a purely random sequence.

(3) When $r_1 > 1$, and $r_2 < 1$

In this case, the propagation reaction types 11 and 21 will be preferred to types 12 and 22, and consequently the probability of M_1 entering; into the copolymer chain will be higher as compared to M_2 monomer. Thus the copolymer formed will be richer in M_1

If r_1 and r_2 differ very widely, the copolymer formed will compromise entirely M_1 and incorporation of M_2 monomer in any appreciable quantity in growing copolymer chain will be very difficult.

(4) When $r_1 < 1$ and $r_2 > 1$

In this case, the copolymer formed will have higher amount of M_2 monomer units. The behaviour in this case will be the opposite of that for case (3).

(5) When $r_1 < 1$ and $r_2 < 1$

In such case, the propagation reaction type 12 and 21 are preferred to types 11 and 22, i.e., while M_2 can add on M_1, M_1 can add on to M_2 at the same time. When r_1 and r_2 are equal, the copolymer formed will be richer in M_1 upto an N_1 value of 0·5 and, then onwards, the copolymer will be richer in M_2. At $N_1 = 0 \cdot 5$, the copolymer will have an nl value of 0·5. It means the copolymer also will have an equal number of M_1 and M_2 components but arranged in random sequence. This composition of the monomer reaction mixture results in the formation of a copolymer with the same monomeric composition, it is called ***'azeotropic composition'***. The value of N_1 can be get from following equation:

$$N_1 = \frac{1 - r_2}{(2 - r_1 - r_2)}$$

(6) When $r_1 > 1$ and $r_2 > 1$

In this case, a mixture of the two homopolymers is formed. Sometimes, block copolymers are formed with long sequences of M_1 followed by a long sequence of M_2

(7) When r_1 or $r_2 = 0$

In this case, a copolymer with a particular azeotropic composition is formed. If the mole fraction of the monomer with a zero reactivity ratio is below the azeotropic composition, the azeotropic copolymer along with comonomer will be formed.

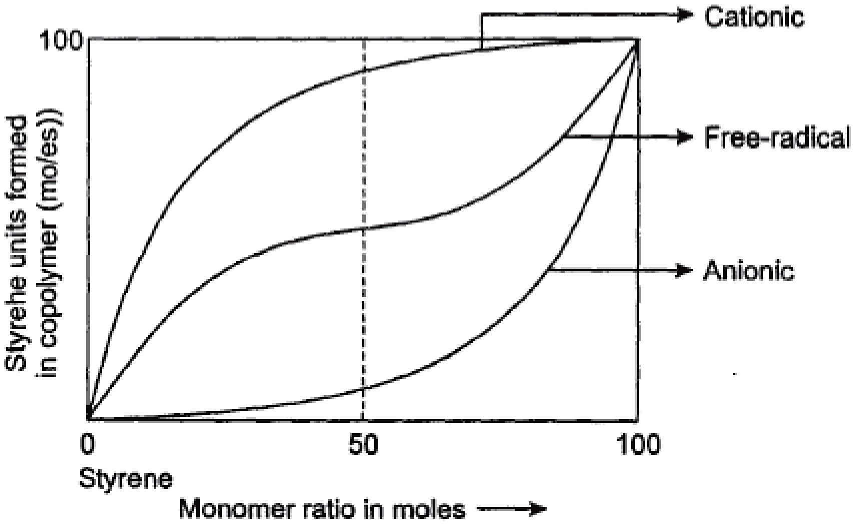
If the mole fraction is more than azeotropic composition, the azeotropic copolymerisation will proceed until the comonomer is consumed and the excess of the monomer with zero activity ratios remains unpolymerised.

(b) Ionic Copolymerisation

In ionic copolymerisation, copolymer is formed by monomer units, which are polymerised by ionic initiators. The fundamental principle of ionic copolymerisation is almost same to free-radical copolymerisation. There is, however, a major difference that in free-radical copolymerisation, the reactivity ratios r_1 and r_2 are dependent only on the monomer pairs M_1 and M_2, and temperature of polymerisation, whereas in ionic copolymerisation, the reactivity ratios dependent not only on the monomer pair and temperature, but also on the solvent and the initiators which are used in that system.

In ionic polymerisation, the reactivity of an ion is extremely dependent on the polarity of the polymerisation system and the reactivity ratios of the same monomer pair at the same temperature can change with the initiator and the solvent used. Since the direction of the cationic or anionic propagation is also directed by the initiator and the solvent system, same monomer pair can further have different reactivity rates depending whether the copolymerisation is cationic or anionic. Since the same monomer pair will have different values of r_1 and r_2 depending on the mode of propagation, by different method the same monomer pair will give copolymers of totally different monomeric compositions. The best example of such type of copolymerisation is the monomer pair methyl methacrylate-styrene.

At an equimolar ratio of styrene to methyl methacrylate, free-radical copolymerisation yields a copolymer (initiated by benzoyl peroxide) using about 50% styrene, while in the cationic copolymerisation (initiated by boron trifluoride etherate) forms a copolymer using more than 95% styrene, and in anionic copolymerisation (initiated by triphenyl methyl sodium) gives a copolymer containing less than 5% styrene. The composition curves are shown:



Curves showing effect of polymerisation types on composition of copolymer formed from the same monomer pair.

(c) Copolycondensation

In polycondensation reaction, a pair of difunctional monomers is brought about to produce a homopolymer. Whereas in copolycondensation reaction, reactants are more than a single pair and resulting in a copolymer.

If A and B are functional groups capable of undergoing condensation reactions, the simple polycondensation and co-polycondensation can be shown as follows:

In simple polycondensation reaction:

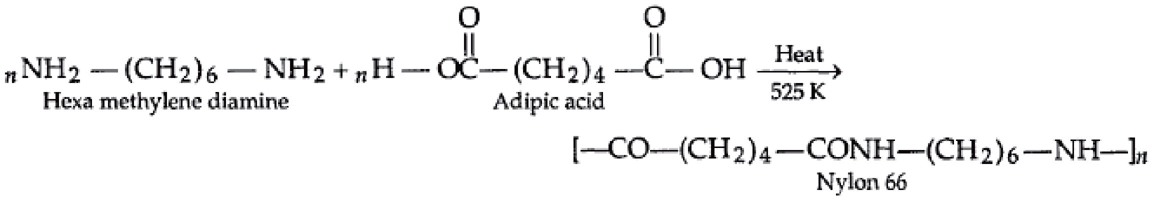
$$A-R-A+B-R'-B \longrightarrow A-R-AB-R'-B+\text{By product}$$

In co-polycondensation reaction:

$$A-R-A+B-R'-B+A-R''-A \longrightarrow A-R-AB-R''-BA-R''-A+\text{By product}$$

Mixed polyamides and mixed polyesters are well known examples of co-polycondensation.

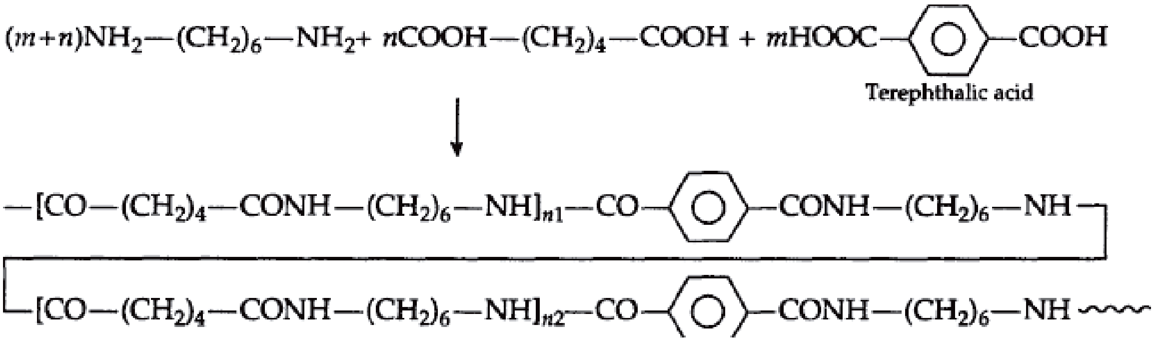
Nylon 6, 6 is a polyamide formed by the polycondensation of hexa methylene diamine and adipic acid.



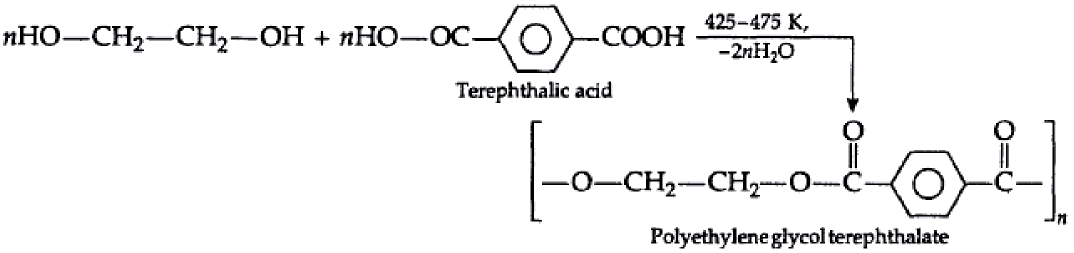
$$\underset{\text{Hexa methylene diamine}}{{}_{n}NH_2-(CH_2)_6-NH_2}+\underset{\text{Adipic acid}}{{}_{n}H-O\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH}\xrightarrow[525\,K]{\text{Heat}}\underset{\text{Nylon 66}}{[-CO-(CH_2)_4-CONH-(CH_2)_6-NH-]_n}$$

Nylon 66 is a tough and crystalline material, which has very low melting point 270°C. If the melting point of this polyamide has to be increased, the terephthalic acid is used to mix in the reaction mixture.

In this case, the copolycondensation reaction is involved and produces a copolymer polyamide with high melting point, and increased crystallinity. This product contains the aromatic nucleus, rather than purely aliphatic chains all through the chain backbone as:

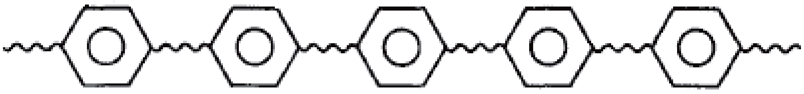


Similarly simple polyester is made from ethylene glycol and terephthalic acid as:



The polyethylene glycol terephthalate is a highly crystalline and rigid copolymer, which is difficult to process due to the presence of a large number of para linked aromatic rings in its chain backbone. When a small amount of dimethyl isophthalate is mixed into the reaction mixture, it forms a copolymer or mixed polyester which consists of para linkages along with meta linkages in the structure. This mixed polyester also contains reduced chain rigidity and crystallinity.

Simple polyester: Polyethylene terephthalate)



Mixed polyester: (Polyethylene terephthalate + dimethyl isophthalate)

(where ∿∿∿ = $—COO—CH_2—CH_2—OCO—$)

7. TYPES OF COPOLYMERS

The copolymerisation involves two monomers. A variety of structures can be obtained even in the simplest case of copolymers. The five important types of existing copolymers are as:

(i) Statistical copolymers: When irregular propagation of monomers, A and B takes place the two units enter the chain in a statistical fashion, thus the statistical copolymers are formed. The most commonly encountered structure of this type is

-(ABBAAAABAABBBA)-

(ii) Alternating copolymers: When equimolar quantities of two monomers are distributed in a regular alternating manner in the chain, the alternating copolymer is formed. For example

-(ABABABA)-

Many of the step-growth polymers are formed by the condensation of two (A - A), (B-B) type monomers. They could be considered as alternating copolymers but these are commonly treated as homopolymers with the repeat unit corresponding to the dimeric residue.

(iii) Block copolymers: The copolymers may also contain long sequences of one monomer joined to another sequence or block of the second. This produces a linear copolymer of form AA - AABBB - B, i.e., an [A] [B] block, but other combinations are also possible as:

A B di block

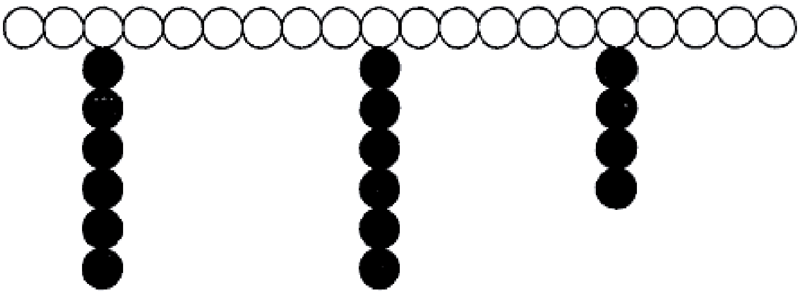
A B A Tri block

B A B Tri block

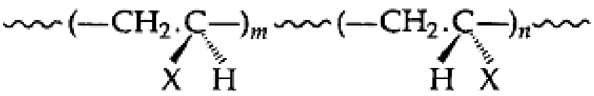
Alternating block

Tappered block

(iv) Graft polymer: This is a non-linear or branched block copolymer which is formed by attaching chains of one monomer to the main chain of another homopolymer.



(v) Stereoblock copolymers: Stereoblock copolymer consists of very special structure which is formed from one monomer where the distinguishing feature is the tacticity of each block, i.e.



$$\sim\sim(-CH_2.\underset{X\quad H}{C}-)_m\sim\sim(-CH_2.\underset{H\quad X}{C}-)_n\sim\sim$$

The block and graft copolymers possess the properties of both homopolymers, whereas the random and alternating structures have characteristics which are more of a compromise between the extremes.

8. INORGANIC POLYMERS

Inorganic polymers are polymers with a skeletal structure that does not include carbon atoms in the backbone. Polymers containing inorganic and organic components are sometimes called hybrid polymers, and most so-called inorganic polymers are hybrid polymers. One of the best known examples is polydimethylsiloxane, otherwise known commonly as silicone rubber. Inorganic polymers offer some properties not found in organic materials including low temperature flexibility, electrical conductivity, and non-flammability The term inorganic polymer refers generally to one-dimensional polymers, rather than to heavily crosslinked materials such as silicate minerals. Inorganic polymers with tunable or responsive properties are sometimes called smart inorganic polymers. A special class of inorganic polymers are geopolymers, which may be anthropogenic or naturally occurring.

Traditionally, the area of inorganic polymers focuses on materials in which the backbone is composed exclusively of main group elements.

Homochain polymers

Homochain polymers have only one kind of atom in the main chain. One member is polymeric sulfur, which forms reversibly upon melting any of the cyclic allotropes, such as S_8. Organic polysulfides and polysulfanes feature short chains of sulfur atoms, capped respectively with alkyl and H. Elemental tellurium and the gray allotrope of elemental selenium also are polymers, although they are not processable.

Polymeric forms of the group IV elements are well known. The premier materials are polysilanes, which are analogous to polyethylene and related organic polymers. They are more fragile than the organic analogues and, because of the longer Si-Si bonds, carry larger substituents. Poly(dimethylsilane) is prepared by reduction of dimethyldichlorosilane. Pyrolysis of poly(dimethylsilane) gives SiC fibers. Heavier analogues of polysilanes are also known to some extent. These include polygermanes, $(R_2Ge)_n$ and polystannanes, $(R_2Sn)_n$.

Heterochain polymers

1. Si-based: Heterochain polymers have more than one type of atom in the main chain. Typically two types of atoms alternate along the main chain. Of great commercial interest are the polysiloxanes where the main chain features Si and O centers, -Si-O-Si-O-. Each Si center has two substituents, usually methyl or phenyl. Examples include polydimethylsiloxane (PDMS, $(Me_2SiO)_n$), polymethylhydrosiloxane (PMHS $(MeSi(H)O)_n$) and polydiphenylsiloxane ($(Ph_2SiO)n$). Related to the siloxanes are the polysilazanes. These materials have the backbone formula Si-N-Si-N-. One example is perhydridopolysilazane PHPS. Such materials are of academic interest.

2. P-based: A related family of well studied inorganic polymers are the polyphosphazenes. They feature the backbone -P-N-P-N-. With two substituents on phosphorus, they are structurally similar related to the polysiloxanes. Such materials are generated by ring-opening polymerization of hexachlorophosphazene followed by substitution of the P-Cl groups by alkoxide. Such materials find specialized applications as elastomers.

3. B-based: Boron-nitrogen polymers feature -B-N-B-N- backbones. Examples are polyborazylenes, polyaminoboranes

4. S-based: The polythiazyls have the backbone -S-N-S-N-. Unlike most inorganic polymers these materials lack substituents on the main chain atoms. Such materials exhibit high electrical conductivity, a finding that attracted much attention during the era when polyacetylene was discovered. It is superconducting below 0.26 K