M.Sc. IV Semester

Chemistry
Paper-IV (Polymers)

POLYMERISATION

Polymerisation is a process which allows simple low molecular weight compounds to combine and forms a complex high molecular weight compound. For this process, each molecule of the compound should have the capability to react at least with two other molecules of the same or some other compound. In other words, they should have a functionality of at least two.

The functionality of a compound depends on the number of its reactive sites. Due to the presence of the reactive functional groups, a compound assumes its functionality. These groups are such as —OH, —COOH, —NH_2, —SH, —NCO, etc. The number of these functional groups per molecule of the compound defines its functionality.

As described earlier, the polymerisation is effected by two processes, *i.e.*, addition and condensation polymerisation. These terms were based on the conventional classification by *Carothers* (1929) and have since been modified by *H.F. Mark* (1950) as chain polymerisation and step polymerisation.

(1) 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 the 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 :

(A) Free-Radical Addition Polymerisation

The polymer chain is initiated by free radicals produced by the decomposition o 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 :

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

The low molecular weight compounds mainly azo, peracids, peroxides, peresters, hydroperoxides are useful as initiators. Initiators can be decomposed and form free radicals while 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 :

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

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

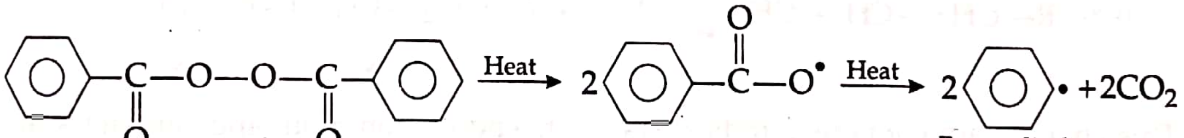
The polymerisation reactions initiated by UV light are known as 'photoinitiated polymerisation'.

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 :

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

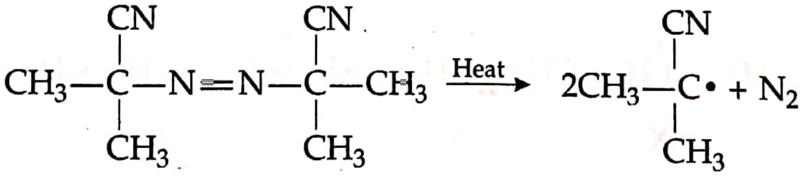
$$\underset{\text{Hydroperoxide}}{R{-}O{-}OH} + Co^{2+} \longrightarrow R\dot{O} + HO^- + Co^{3+}$$

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



Benzoyl peroxide

Free-radicals

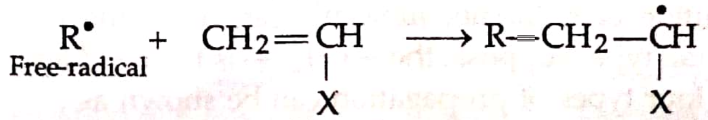


$$\underset{\text{Azo bis isobutyro nitrile}}{CH_3{-}\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}N{=}N{-}\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CH_3} \xrightarrow{\text{Heat}} \underset{\text{Free radicals}}{2CH_3{-}\overset{\overset{CN}{|}}{\underset{\underset{CH_3}{|}}{C}}\bullet} + N_2$$

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

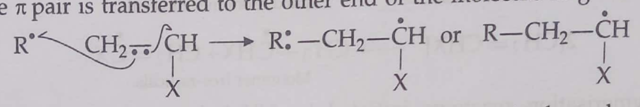
The rate of decomposition of these initiators depends on the reaction temperature, solvents used, and the intensity and wavelength of the radiations.

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 :



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

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 π electrons are not very close 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 :

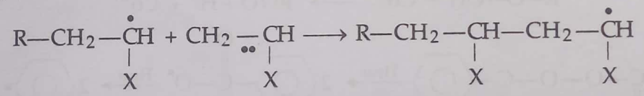


$$R^{\bullet} + \underset{}{CH_2}{=}\underset{X}{\underset{|}{CH}} \longrightarrow R{:}-CH_2-\underset{X}{\underset{|}{\dot{C}H}} \text{ or } R-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

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 π 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.*

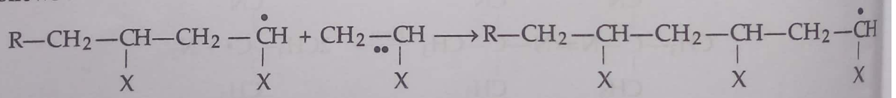
PROPAGATION

After initiation step, the propagation step get 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 :



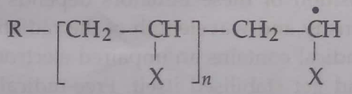
$$R-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

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 :



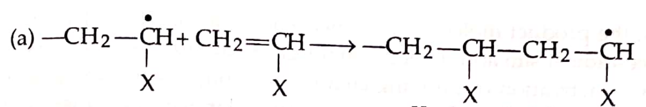
$$R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow R-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

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 :



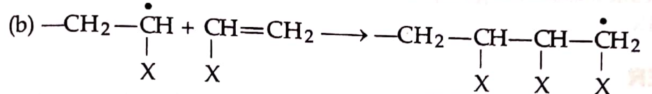
$$R-\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_n-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

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 :



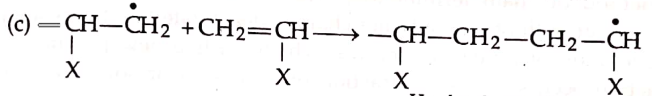
$$\text{(a)}\ -CH_2-\overset{\bullet}{\underset{X}{CH}}+CH_2=\underset{X}{CH}\longrightarrow -CH_2-\underset{X}{CH}-CH_2-\overset{\bullet}{\underset{X}{CH}}$$

Head-to-tail addition



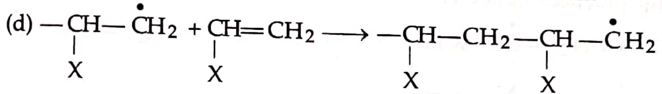
$$\text{(b)}\ -CH_2-\overset{\bullet}{\underset{X}{CH}}+\underset{X}{CH}=CH_2\longrightarrow -CH_2-\underset{X}{CH}-\underset{X}{CH}-\overset{\bullet}{\underset{X}{CH_2}}$$

Tail-to-tail addition



$$\text{(c)}\ =\underset{X}{CH}-\overset{\bullet}{CH_2}+CH_2=\underset{X}{CH}\longrightarrow -\underset{X}{CH}-CH_2-CH_2-\overset{\bullet}{\underset{X}{CH}}$$

Head-to-head addition

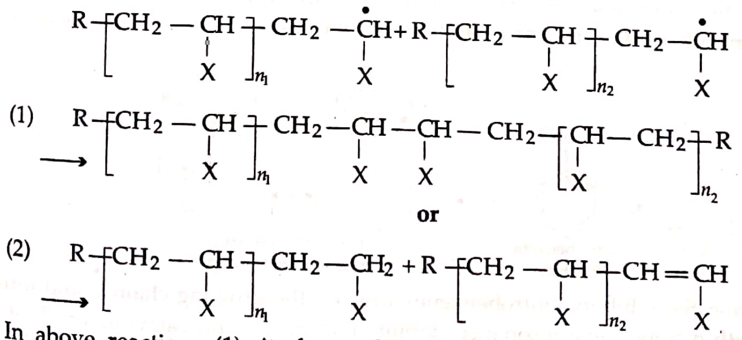


$$\text{(d)}\ -\underset{X}{CH}-\overset{\bullet}{CH_2}+\underset{X}{CH}=CH_2\longrightarrow -\underset{X}{CH}-CH_2-\underset{X}{CH}-\overset{\bullet}{CH_2}$$

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 :



$$R\left[CH_2-\underset{X}{CH}\right]_{n_1}CH_2-\overset{\bullet}{\underset{X}{CH}}+R\left[CH_2-\underset{X}{CH}\right]_{n_2}CH_2-\overset{\bullet}{\underset{X}{CH}}$$

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

or

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

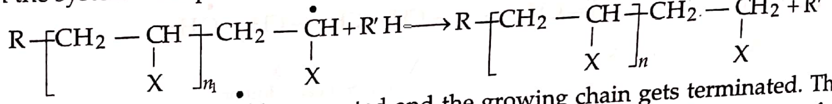
In above reactions (1), it shows that the two chains combine by the coupling of unpaired electrons and form a sigma bond. Such type of termination is called **'termination by coupling'** because this process involves the coupling of the one lone pair of electrons.

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 produc does not consist of any free-radical site and, hence, cannot grow any further. The process o termination thus causes in deactivation of growing chain. The groups which are present a the end of the chain are called the **'end groups'**. For example, in above cases, these group are —R, and —CH_2=CHX.

CHAIN TRANSFER

There is another method of chain termination, which takes place by the **'transfe 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 chai growth. The transfer reaction occurs by the abstraction of a H-atom or some other aton present in the system. This process follows as :

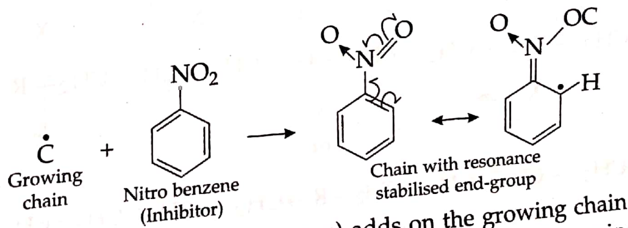


$$R\!\left[CH_2-\underset{X}{CH}\right]_{n_1}\!-CH_2-\underset{X}{\dot{C}H}+R'H \longrightarrow R\!\left[CH_2-\underset{X}{CH}\right]_n\!-CH_2-\underset{X}{CH_2}+\dot{R}'$$

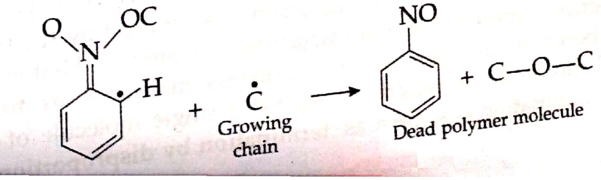
Now, a new free-radical $\dot{R}'$ is generated and the growing chain gets terminated. Thus $\dot{R}'$ is ready to initiate as well as propagate a fresh chain growth. Here, the termination of on chain growth and the initiation of a new one takes place simultaneously. Since the chai growth is transferred 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 o 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 Ċ 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 :

$$\underset{\text{Growing chain}}{\overset{\bullet}{C}} + \overset{\bullet}{O}—\overset{\bullet}{O} \longrightarrow C—O—\overset{\bullet}{O}$$

$$C—O—\overset{\bullet}{O} + \overset{\bullet}{C} \longrightarrow C—O—O—C$$

(B) Ionic Polymerisation

The ionic polymerisation is divided into two categories :

(i) Cationic polymerisation

(ii) Anionic polymerisation

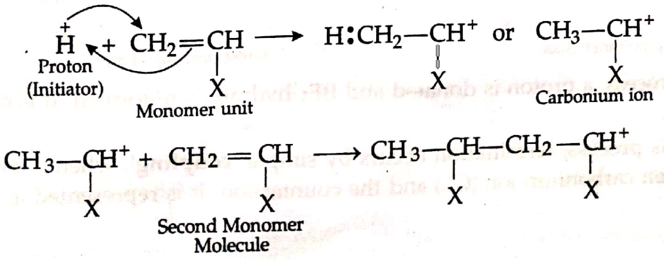
(i) Cationic Polymerisation

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.

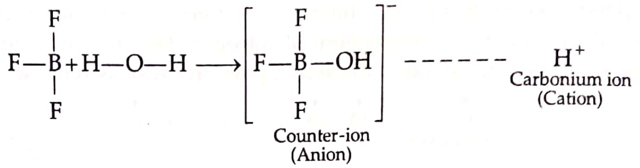
The mechanism of this polymerisation involves an attack on the π electron pair of the monomer molecule. In the chain reaction, first a proton is introduced into a monomer. The proton attracts the π electron pair towards it and a positive charge of the proton is transferred to the end of the monomer molecule; 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 :



$$\underset{\substack{\text{Proton}\\ \text{(Initiator)}}}{\overset{+}{H}} + \underset{\text{Monomer unit}}{CH_2{=}\underset{|}{\underset{X}{CH}}} \longrightarrow H{:}CH_2—\underset{X}{\underset{\|}{CH^+}} \text{ or } \underset{\text{Carbonium ion}}{CH_3—\underset{X}{\underset{|}{CH^+}}}$$

$$CH_3—\underset{X}{\underset{|}{CH^+}} + \underset{\substack{\text{Second Monomer}\\ \text{Molecule}}}{CH_2 = \underset{X}{\underset{|}{CH}}} \longrightarrow CH_3—\underset{X}{\underset{|}{CH}}—CH_2—\underset{X}{\underset{|}{CH^+}}$$

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 :

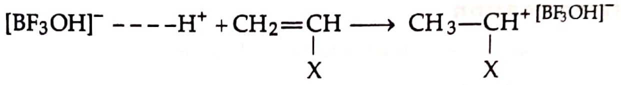


$$BF_3 + H{-}O{-}H \longrightarrow [F_3B{-}OH]^- \text{ ------ } H^+$$

Counter-ion (Anion)

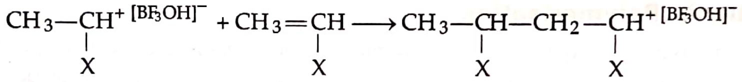
Carbonium ion (Cation)

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 :

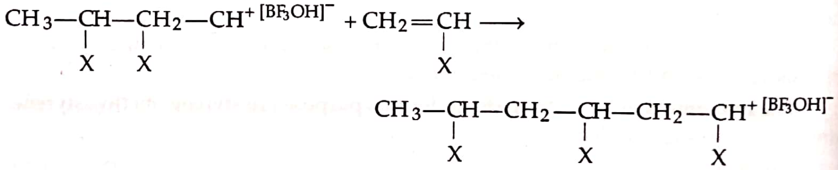


$$[BF_3OH]^- \text{----} H^+ + CH_2{=}\underset{X}{CH} \longrightarrow CH_3{-}\underset{X}{CH^+}[BF_3OH]^-$$

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 :



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



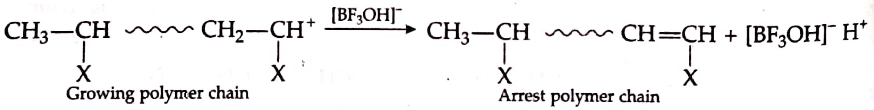
$$CH_3{-}\underset{X}{CH}{-}\underset{X}{CH_2}{-}CH^+[BF_3OH]^- + CH_2{=}\underset{X}{CH} \longrightarrow$$

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

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 :



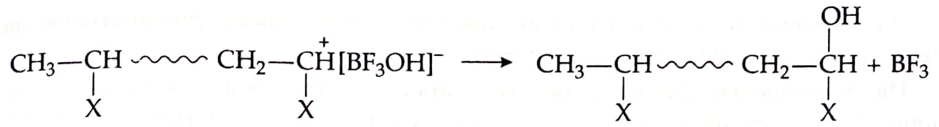
$$CH_3{-}\underset{X}{CH} \sim\sim CH_2{-}\underset{X}{CH^+} \xrightarrow{[BF_3OH]^-} CH_3{-}\underset{X}{CH} \sim\sim CH{=}\underset{X}{CH} + [BF_3OH]^- H^+$$

Growing polymer chain

Arrest polymer chain

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 :

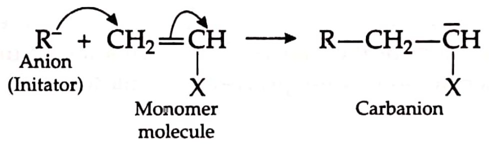


$$\underset{\mathrm{X}}{\mathrm{CH_3{-}CH}} \sim\sim \mathrm{CH_2}{-}\underset{\mathrm{X}}{\overset{+}{\mathrm{CH}}}[\mathrm{BF_3OH}]^- \longrightarrow \underset{\mathrm{X}}{\mathrm{CH_3{-}CH}} \sim\sim \mathrm{CH_2}{-}\underset{\mathrm{X}}{\overset{\mathrm{OH}}{\mathrm{CH}}} + \mathrm{BF_3}$$

(ii) Anionic Polymerisation

In anionic polymerisation, a negatively charged ion attacks on π 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 :

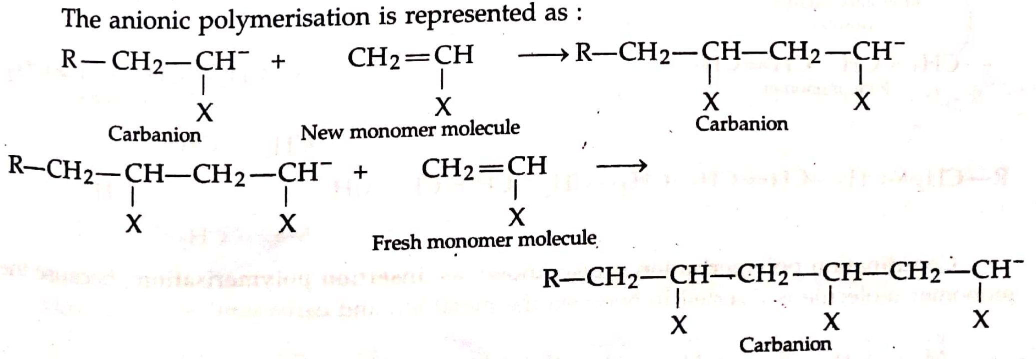


$$\mathrm{R^-} + \mathrm{CH_2{=}}\underset{\mathrm{X}}{\mathrm{CH}} \longrightarrow \mathrm{R{-}CH_2{-}}\underset{\mathrm{X}}{\bar{\mathrm{C}}\mathrm{H}}$$

Now the **propagation** process starts. It is initiated by newly formed carbanion, which attacks on the second monomer unit. Thus the π 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 π 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 all the 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 initiates 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 :



$$\mathrm{R{-}CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}^-} + \mathrm{CH_2{=}}\underset{\mathrm{X}}{\mathrm{CH}} \longrightarrow \mathrm{R{-}CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}^-}$$

$$\mathrm{R{-}CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}^-} + \mathrm{CH_2{=}}\underset{\mathrm{X}}{\mathrm{CH}} \longrightarrow \mathrm{R{-}CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{{-}CH_2{-}}\underset{\mathrm{X}}{\mathrm{CH}^-}$$

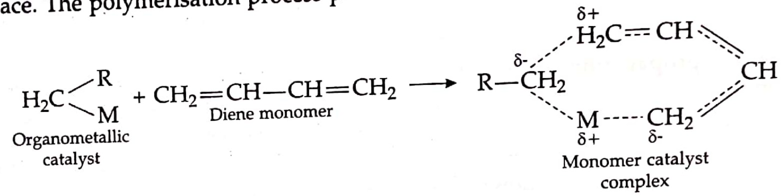
In this case the initiators used are generally the organo-alkali compounds such as ethyl sodium, butyl lithium, triphenyl methyl potassium. Similarly, alkali metal amides, hydroxides and alcoxides can also be used for the anionic polymerisation process.

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

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

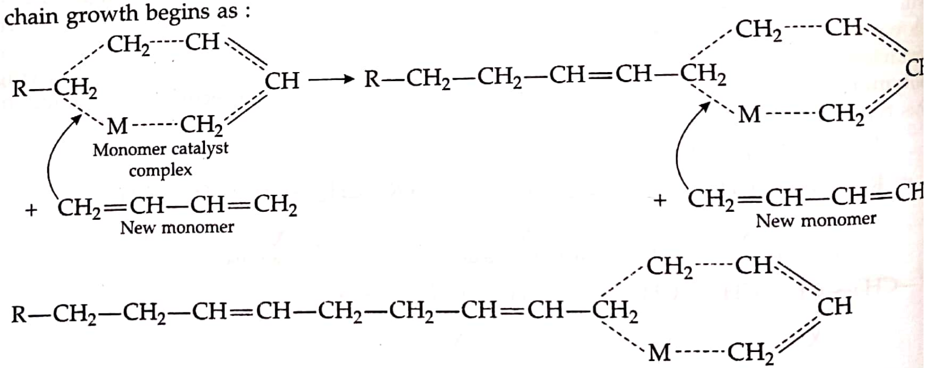
(C) Coordination Polymerisation

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

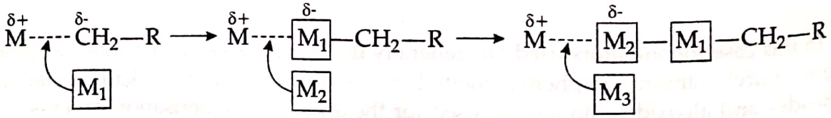


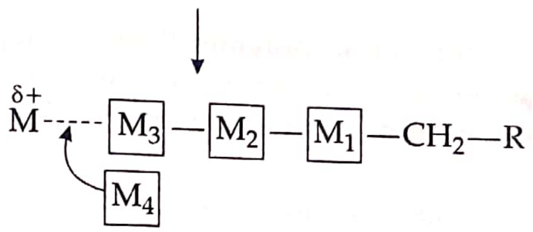
where, M = Transition metals such as Ni, Cr, Mo, V, Ti or Rh.

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



Coordination polymerisation is also known as **'insertion polymerisation'**, because t monomer molecule is inserted in between the metal ion and carbanion.

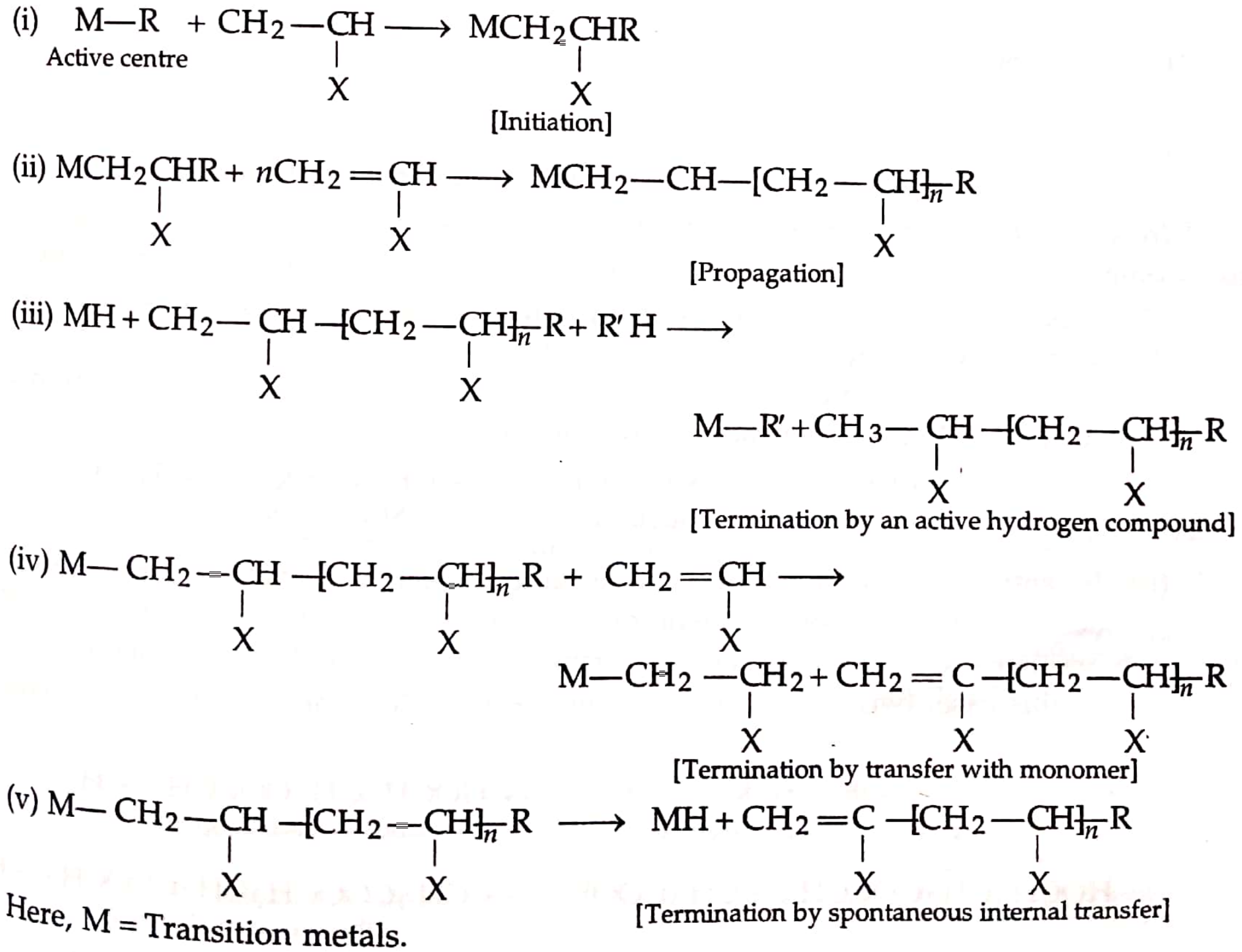




Here, M = metal ion, and M_1, M_2, M_3, M_4, etc., are the first, second, third and fourth monomer units which are added to the polymer growing chain.

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

[Initiation]

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

[Propagation]

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

$M{-}R' + CH_3{-}\underset{X}{\underset{|}{CH}}{-}[CH_2{-}\underset{X}{\underset{|}{CH}}]_n{-}R$

[Termination by an active hydrogen compound]

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

$M{-}CH_2{-}\underset{X}{\underset{|}{CH_2}} + CH_2{=}\underset{X}{\underset{|}{C}}{-}[CH_2{-}\underset{X}{\underset{|}{CH}}]_n{-}R$

[Termination by transfer with monomer]

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

[Termination by spontaneous internal transfer]

Here, M = Transition metals.

(2) Condensation (Step) Polymerisation

In condensation or step polymerisation reaction, the reaction takes place in a step-wise manner and the polymer is formed through a reaction between functional groups of the monomers. Formation of polymer through step polymerisation is a slow process, while chain (addition) polymerisation, chain growth is very fast. Step polymerisation is condensation reaction, where small molecules of water, methanol or ammonia etc., elimina out.

There are many known reactions which can be used in step polymerisation, few them are condensation, ring-opening, amidation, addition and ester-interchange reactio described as follows :

(a) Polycondensation

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

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

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

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

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

In polycondensation, basic reactions are the same as between various reacti 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 water molecule. It should be noted that in this reaction, both the functional grou are consumed and forms an unreactive ester functional group, which can not rea further with any other monomer molecules.

$$\underset{\substack{\text{Methyl alcohol}\\\text{(one hydroxyl group)}}}{CH_3OH} + \underset{\substack{\text{Acetic acid}\\\text{(Carboxylic group)}}}{HOOC{-}CH_3} \longrightarrow \underset{\substack{\text{Methyl acetate}\\\text{(ester group)}}}{CH_3COOCH_3} + H_2O$$

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

$$\underset{\substack{\text{Ethylene glycol}\\\text{(2 hydroxyl groups)}}}{CH_2OH{-}CH_2OH} + \underset{\substack{\text{Acetic acid}\\\text{(1 carboxyl group)}}}{HOOC{-}CH_3} \longrightarrow \underset{\text{Ethylene monoacetate glycol}}{HOCH_2CH_2OOCCH_3} + H_2O$$

$$HOCH_2CH_2OOCCH_3 + CH_3COOH \longrightarrow \underset{\text{ethylene glycol diacetate}}{CH_3COOCH_2CH_2COOCH_3} + H_2$$

(iii) In this case, two molecules each of ethylene glycol and adipic acids are taken f the polycondensation reaction and form a monoester in first step. This produ still consists of two reactive groups, *i.e.*, one hydroxyl and one carboxyl, which c further react with one more molecule of ethylene glycol or adipic acid and give 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 :

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

$$HO—[CH_2—CH_2COO—(CH_2)_4COO]_2—H + \underset{\text{3 molecules}}{3H_2O}$$

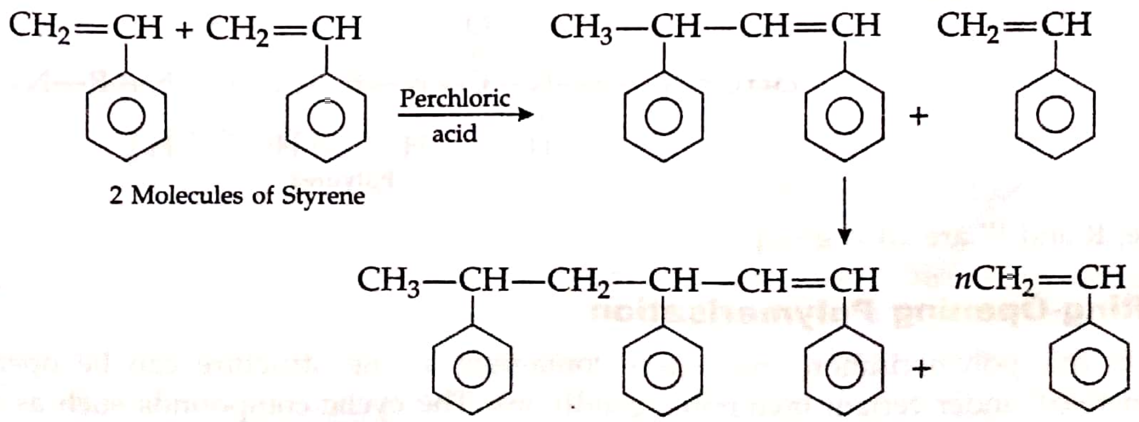
(b) Polyaddition Polymerisation

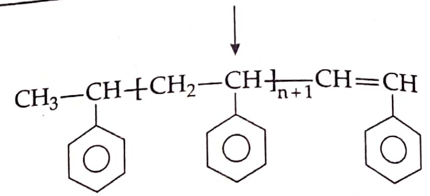
In polyaddition polymerisation, atoms are migrated from one monomer molecule to another. The monomer pairs with reactive functional groups can undergo polyaddition polymerisation.

A vinyl monomer, e.g., styrene, can be a good example of such type of polymerisation. Here, polymer is formed in the presence of perchloric acid. It is a simple addition reaction at the double bond, where any free-radical, carbonium ion, carbanion and elimination of small molecules do not occur.

As against the rapid chain growth in chain polymerisation, polymer growth in polyaddition reaction is rather gradual and is brought about step by step manner. The process involves in following way :

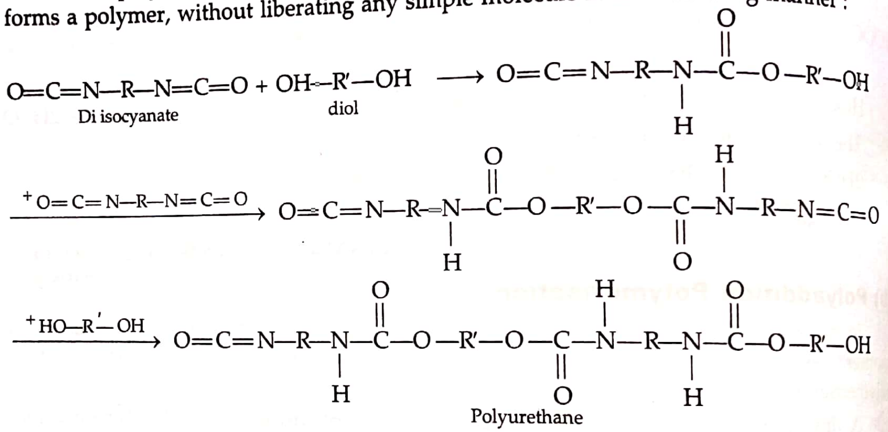
It is interesting to note that intermediate products also contains a double bond between





carbon atoms and, hence, have same reactivity and structural similarity as the starting monomer. Unlike chain polymerisation, in polyaddition reaction, the intermediate product is quite stable and can be isolated from the reaction mixture.

In the polyaddition reaction a pair of monomers containing reactive functional groups forms a polymer, without liberating any simple molecule in the following manner :



$$\underset{\text{Di isocyanate}}{O{=}C{=}N{-}R{-}N{=}C{=}O} + \underset{\text{diol}}{OH{-}R'{-}OH} \longrightarrow O{=}C{=}N{-}R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}OH$$

$$\xrightarrow{+O{=}C{=}N{-}R{-}N{=}C{=}O} O{=}C{=}N{-}R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}O{-}\underset{O}{\underset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}N{=}C{=}O$$

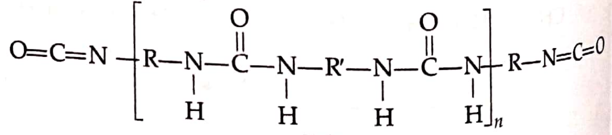
$$\xrightarrow{+HO{-}R'{-}OH} O{=}C{=}N{-}R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}O{-}\underset{O}{\underset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}OH$$

Polyurethane

In above case, the hydrogen atom from the hydroxyl group of the diol migrates and adds on to the nitrogen of the isocyanate group.

In another example of polyaddition reaction, polyurea is formed by monomers such as polyamines and polyisocyanates. Polyurea is a very high molecular weight compound, which is formed by the migration of a highly mobile hydrogen atom of an amino group as follows :

$$_{n+1}\underset{\text{Polyisocyanates}}{O{=}C{=}N{-}R{-}N{=}C{=}O} + {}_{n}\underset{\text{Polyamines}}{H_2N{-}R'{-}NH_2} \longrightarrow$$



$$O{=}C{=}N\left[R{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\underset{|}{N}}{-}R'{-}\underset{H}{\underset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\underset{H}{\underset{|}{N}}\right]_n R{-}N{=}C{=}O$$

Polyurea

where, R and R′ are alkyl groups.

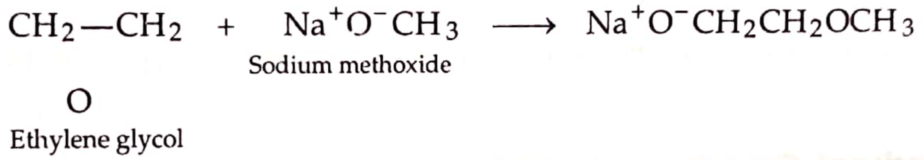
(c) Ring-Opening Polymerisation

In this polymerisation, monomers containing a ring structure can be opened and polymerised 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 :

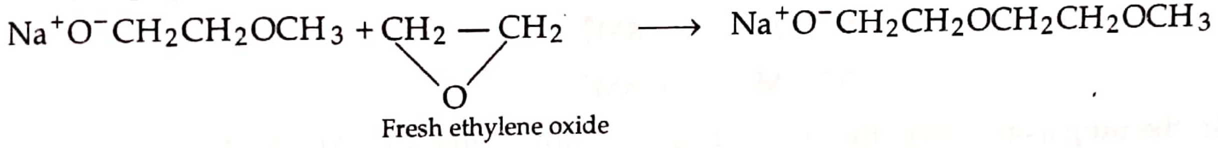
Initiation



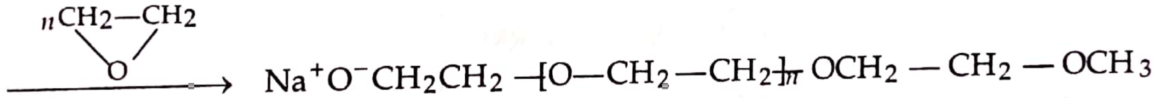
$$CH_2{-}CH_2 + Na^+O^-CH_3 \longrightarrow Na^+O^-CH_2CH_2OCH_3$$

After initiation, 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



$$Na^+O^-CH_2CH_2OCH_3 + CH_2{-}CH_2 \longrightarrow Na^+O^-CH_2CH_2OCH_2CH_2OCH_3$$



$$\xrightarrow{n\,CH_2-CH_2} Na^+O^-CH_2CH_2 {+}O{-}CH_2{-}CH_2{+}_n OCH_2-CH_2-OCH_3$$

After propagation, the termination step started, where HCl is added. HCl 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 π electron pair of the C$=$C bond.

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