

1. INTRODUCTION

Polymerization involves a process in which some reactions is repeated until a compound of very high molecular weight is formed. If repeating units or monomers are chemically similar, the resulting macromolecule will be called homopolymer, while different reacting monomers will yield a copolymer.

1.1. Types of polymerization:

Mainly the process of polymerization can be classified into two heads.

- (a) addition polymerization and
- (b) condensation polymerization.

1.1.1. Addition polymerization:

In this synthesis, the reactive monomers are successively linked together at the site of double bonds or unsaturation. (1-2) Addition polymerization is brought about usually by the opening of a double bond. The bond may be between carbon and carbon, carbon and oxygen, carbon and nitrogen, carbon and sulphur or carbon and silicon. The reaction may also be brought by opening of a ring that consists of three singly bonded atoms of the elements, carbon, nitrogen, oxygen, silicon and sulphur. Generally the multiple bond in the monomer molecule is the site of initiating

the reaction and the chain grows by successive addition of the monomer molecule until conditions are reached where the growth ends.

Addition polymerization can be achieved by two different ways namely: by

- (a) Ionic polymerization and
- (b) Free radical polymerization.

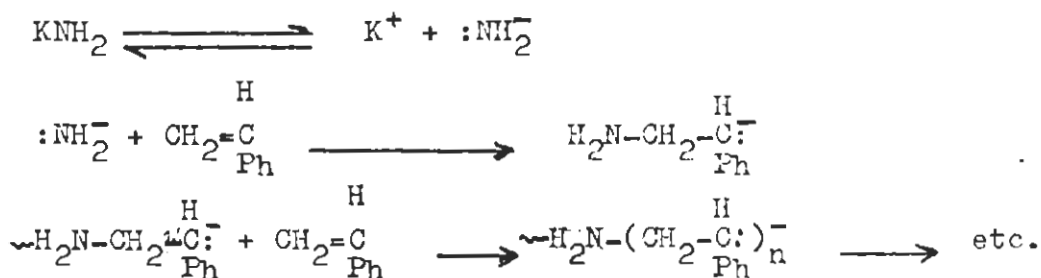
1.1.1.1. Ionic polymerization:

The ionic polymerization is one in which the active end of the growing polymer molecule is either a positive or a negative ion. In the former case where the active end is a positive ion (Carbonium ion), the polymerization is termed as Cationic polymerization. In the latter case where the active end is negative (Carbanion), it is called anionic polymerization. All substituents which cause ionic polymerization are characterized by strong affinity for an electron pair. Substituent groups e.g., alkyl, aryl, ethyl groups etc., promote the release of electrons and therefore monomers that contain such groups are most readily polymerized by ionic or electrophilic catalyst. The Catalysts effective in cationic polymerization are compounds or elements capable of accepting electrons readily. A particular example of this group is boron trifluoride which complexes with water and many other hydrogen containing molecules like inorganic solvents which dissociates into proton, H^+ and the negative charged

counterion $[\text{BF}_3\text{OH}^-]$ or $[\text{BF}_3\text{X}^-]$. The resulting proton attacks the double bond of the monomer and initiates the reaction as can be seen by the following equation (3):



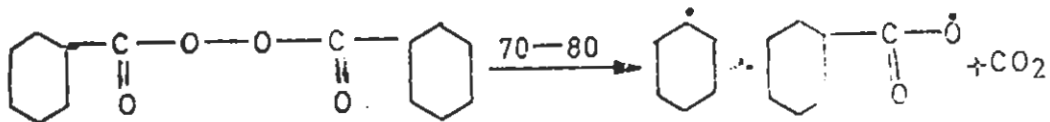
Alkali metals, amide ions (from alkali metals dissolved in liquid ammonia), metal alkyls, Grignard reagents etc. can initiate the anionic type of polymerization. Carbanions are formed in the first instance which propagates the chain reaction as follows:



An example of anionic polymerization is the polymerization of styrene by butyl lithium (4),



undergo addition polymerization by a free radical mechanism. The free radicals are formed by the homolytic fission of a covalent bond. The unpaired electron which characterizes a free radical does not impart any charge to the species (6).

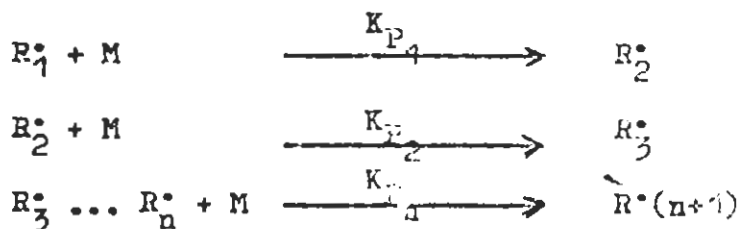


Fission of covalent bonds may be achieved thermally (in the presence or absence of catalysts) or by photo-chemical reactions, high energy irradiation and by mechanical means.

In the simplest, free radical polymerization is accomplished mainly by the following three steps viz. the initiation, propagation and termination. In the initiation step, an active centre is produced which possesses great reactivity.

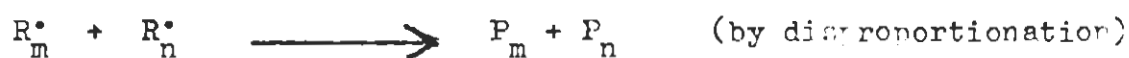
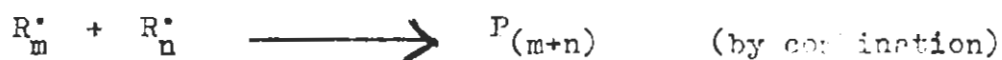


The propagation step leads the attack of a free radical upon the double bonds of a monomer in successive series of reactions,



The termination involves the mutual saturation of the growing

chain free radicals by coupling or disproportionation⁽⁷⁾



where P_m and P_n represent dead polymer molecules containing m & n monomer units respectively. R_m^\bullet & R_n^\bullet indicate the growing polymer radicals.

Beside these steps, other reaction steps such as chain transfer, branching or cross-linking can also take place in certain cases.

Chain transfer step:

In addition to the normal chain growing process, the activity may be transferred from the growing polymer to monomer (M) or solvent (S) molecules,



This concept was first introduced by Flory⁽⁷⁾. As a matter of fact it does not destroy the growth process but decreases the average degree of polymerization.

1.1.2. Condensation polymerization:

In this polymerization synthesis the monomer bearing two or more reactive groups react intermolecularly to form a large molecule. Elimination of a small molecule takes place simultaneously

as a by product which is usually nitrogen hydrogen, water hydrogen chloride etc. Condensation polymerization proceeds through a wide variety of steps leading to different types of end product (8-11). In a simple case of the polyesterification of a hydroxy acid the first step is the formation of a dimer by intermolecular esterification,



This step is followed by second similar process in which further molecules of monomers react to give a dimer or trimer. The dimer may react with another dimer to form a tetramer. The reaction of growing polymer is a propagation and not a termination reaction since the new molecule still bear reactive terminal as obvious in above reaction. Polyester, Polyamides, polyenhydrides, polysulphides, silicon etc. are all prepared by employing condensation polymerization. Synthesis of very high molecular weight polymers is however limited with condensation polymers.

1.2. Factors affecting the polymerization:

The conditions under which the polymerizations are performed is very important. There are many significant variables that affect the polymerization. Some of them are temperature, catalyst, purity of monomers, solvent etc. The final properties of the polymers depend upon the amount of catalyst used. High concentration of

catalyst increases the rate of polymerization but decreases the molecular weight.

1.2.1. Temperature:

The variation of rate constants of a chemical reaction varies with temperature and quantitatively is governed by the Arrhenius equation:

$$K = Ae^{-E/RT}$$

Where A, E and T are collision factor, activation energy and temperature (absolute) respectively. This type of temperature dependence can be interpreted in terms of collision theory. During a polymerization reaction, the movement of monomer molecules increases with the rise in temperature resulting in the enhancement of yield. Velocity coefficient of the reaction also depends upon temperature. Typical values for the overall velocity coefficient (K_p) obtained with various initiator at different temperature are shown in table 1.1.

TABLE - 1.1

Catalyst	Temperature °C	K_p mol ⁻¹ lse ⁻¹	Reference
Benzoyl peroxide	30	9.06 x 10 ⁻⁶	12
Benzoyl peroxide	60	223.0 x 10 ⁻⁶	13
Benzoyl peroxide	90	2710 x 10 ⁻⁶	12
Azobisisobutyronitrile	50	100 x 10 ⁻⁶	14
Azobisisobutyronitrile	60	30 x 10 ⁻⁶	13
Azobisisobutyronitrile	77	138 x 10 ⁻⁶	14

Bevington et al⁽¹⁵⁾ reported that ratio of disproportionation to combination (K_t'/K_t) in the termination reaction for methyl methacrylate also depends upon temperature. The values of K_t'/K_t was found 1.5 at 0°C while at temperatures 25°C and 60°C these were 2.13 and 5.75 respectively. According to the observation of Matheson et al⁽¹⁶⁾ and Mackey and Melville⁽¹⁷⁾, the velocity coefficients for propagation in acetate polymerization increase with the rise in temperature. Roche and Price⁽¹⁸⁾ reported that in thermal polymerization of styrene, the initial rate is about 0.1% per hour at 60°C, 1.0 percent per hour at 90°C and 8% per hour at 120°C showing the decrease in rate with decrease in temperature. Burnett and Wright⁽¹⁹⁾ carried out the photosensitized homogeneous polymerization of vinyl chloride in tetrahydrofuran between 25°C and 55°C. They found that at the lower temperature, the rate of polymerization is proportional to $(M)^{1.5}$ and the square root of the sensitizer concentration but at temperature higher than 25°C, the rate is proportional to a power of sensitizer concentration of approximately 0.6 and to a power of the intensity varying from 0.6 to 0.9. It is thus obvious that temperature is a significant variable in the polymerization reaction.

1.2.2. Catalyst:

Catalyst helps in producing active centres for initiating the polymerization reaction. The rates of polymerization depends upon the nature and the concentration of catalyst. It is not possible to produce active centres thermally at low temperatures. This requires more energy which may be achieved only by attaining

higher temperature. Active centres at low temperatures can however only be produced by the addition of proper catalyst. Peroxides, persulphates, azocompounds, Friedel crafts catalysts, Ziegler Natta catalysts, Organometallic compounds are some of the well known catalysts in use for carrying out polymerization. In addition to these, some metal complexes⁽²⁵⁻²⁸⁾ and inorganic salts e.g., $ZnCl_2$, $CoCl_2$ etc. have also been introduced as a source of free radicals. The effect of concentration of these catalysts on the rate of polymerization has been investigated to report the relationships of the two variables in the form of mathematical equation:

$$- \frac{d[M]}{dt} = K_M [M] \text{Cat}^{1/2}$$

1.2.3. Solvent:

Solvent in polymerization reaction always play a significant role and act itself as a heat transfer medium. The polymerization in the presence of the solvent is more uniform than mass polymerization since the presence of the solvent permits agitation during polymerization which eliminates local reactions and over heating. On account of these advantages, solvents affect the rate of polymerization and molecular weight of polymer formed. Since the conformations of the macromolecules in solvent depends on the type of the solvent used in the system, the nature of the solvents also accounts much in polymerization reaction. A poor solvent may impede the approaching reagent thus showing of inhibiting reaction. A good solvent on the other hand will facilitate the reaction since

it will not prevent access of the approaching reagent. It is generally observed that the polymers of lower molecular weight may be obtained by polymerizing the monomers in the solvent bearing the lower molecular weight and vice versa.

1.2.4. Purity of monomers:

Trace impurities in catalysed or uncatalysed polymerization have a marked effect on the properties of the resulting product. Once the macromolecules are contaminated and attached with the unwanted product present as impurity of the monomers, the purification becomes tedious and cumbersome. Often, the undesirable products may lead to crosslinking reactions with the eventual formation of gel. Another serious disadvantage of contamination of the macromolecules may give rise to degradation of the polymer continuously. Consequently the physical properties of the polymers no longer remain unaffected and deterioration is observed in most of the bulk properties of the contaminated polymers. Thus the presence of solvent in concentration as little as 1 percent in a polymer may drop its glass transition temperature upto 7°C (31-33). The tensile strength is also affected similarly since the impurity will tend to act as plasticizer. Anomaly in rate of polymerization of certain polymers has also been attributed to the concentration of the monomers.

In the light of the above comments, the criteria of purity of the monomers must always be kept in mind before undertaking

study of a polymerization system.

1.3. Copolymerization

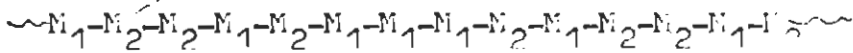
Interest in changing properties of homopolymer by copolymerization dates back since the year 1914. When it was found by Klattle⁽³⁴⁾ that the copolymerization of vinyl esters have different physical and chemical properties. The subject developed rapidly also by knowing the fact that even those monomers which are difficult to homopolymerize can be copolymerized easily in presence of other monomers⁽³⁵⁻³⁷⁾.

The formation of copolymers basically is the binding of the different monomers in the same polymer chain. The binding of the monomers in the same polymer chain is even not restricted to two monomers, it can also be extended to three monomers⁽³⁸⁻⁴²⁾. In the latter case terpolymers are formed. Some examples of the copolymers and terpolymers which have found large use in industry are high impact polystyrene and styrene based acrylonitrile and butadiene copolymers.

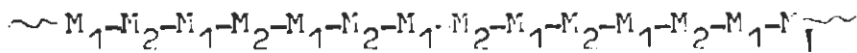
1.3.1. Classification of copolymers:

Four general groups based on the arrangement of monomer units in the common chain can classify a copolymer. These are (a) random copolymers (b) alternate copolymers (c) graft copolymers and (d) block copolymers. If the arrangement of

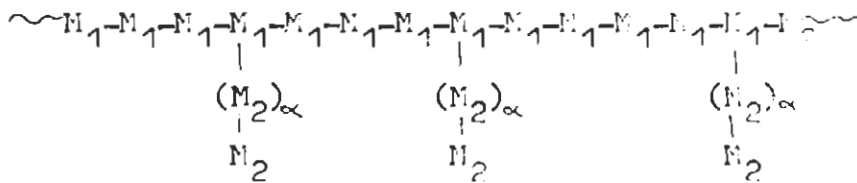
monomer units is more or less random along the chain represents a molecule of random copolymer.



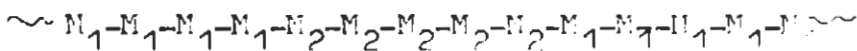
In alternate copolymers, of arrangement of the two units in the chain takes place alternatively,



Graft copolymers contain polymer chains carrying branches of another polymer or copolymer,



Strictly speaking block copolymers are graft copolymers in which a sequence of units of each type is placed together in the common copolymer chain side by side,



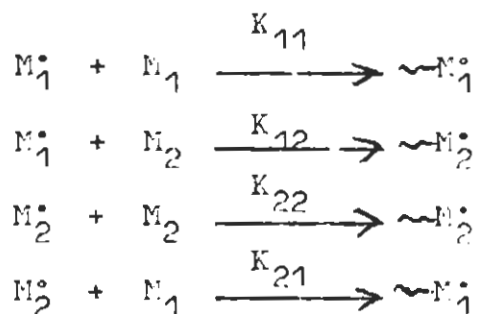
There are differences in properties of the different type of copolymers. Block copolymers are on the whole less interesting than random polymers because the properties of block polymers are by and large, the properties to be expected for a mixture of the component homopolymers. The properties of random copolymers on the other hand can not ordinarily be predicted from properties of the component homopolymer. Block and graft polymers have attraction for the fact that these polymers have

properties corresponding to the properties of mixed polymers without the disadvantages of phase separation.

1.3.2. Characterization of the copolymers:

Although some modern techniques namely electron microscopy, DSC and NMR spectroscopy have been introduced recently which can characterize specifically the order of arrangement of the two units in the common chain of the copolymers, there are some routine methods which may also provide the desired information of the structure of the copolymers. Among these methods mention of the copolymer equation and the monomer reactivity ratio will be considered now.

The copolymer equation (43-45) is important to predict the composition of copolymers at any ratio of conversion in the radical polymerization of the two monomers M_1 and M_2 . The complete scheme comprised of mainly homo- and heteropolymerization reactions as follows:



Where K_{11} , K_{22} are rate constants for the self-propagating reactions and K_{12} and K_{21} are similarly rate constants for cross

propagating reactions. The rate of consumption of the two monomers from the initial reaction mixture can be given separately by following equation,

$$\frac{d[M_1]}{dt} = -K_{11}[M_1^{\cdot}][M_1] - K_{21}[M_2^{\cdot}][M_1] \quad \text{----- (2)}$$

$$\frac{d[M_2]}{dt} = -K_{12}[M_1^{\cdot}][M_2] - K_{22}[M_2^{\cdot}][M_2] \quad \text{----- (3)}$$

The copolymer equation can then be derived from the above equations assuming steady state conditions when,

$$K_{21}[M_2][M_1^{\cdot}] = K_{12}[M_1][M_2^{\cdot}] \quad \text{----- (4)}$$

This equation is represented as,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad \text{----- (5)}$$

$r_1 = \frac{K_{11}}{K_{12}}$ and $r_2 = \frac{K_{22}}{K_{21}}$ are the relative reactivity

ratios i.e. the ratio of the reactivity of the propagating species with its own monomer to the reactivity of the propagating species with the other monomers. In the case, the values of r_1 and r_2 are known with the help of copolymer equation (5) it would be possible to calculate the amount of individual monomers

incorporated in the chain from a given reaction mixture or feed. In turn the reliable values of reactivity ratios can be obtained by analysing the composition of the copolymer formed from a number of runs of mixture of the two monomers varying in $[M_1]/[M_2]$ ratios.

1.3.3. Copolymer Structure and reactivity ratios:

Reactivity ratios influence the structure of the copolymer and as described below may be useful to provide information of order of arrangement of the monomer units in the chain of Copolymer. The influence of the reactivity ratios on the structure of the copolymer can be best illustrated by choosing various combinations of r_1 and r_2 values and showing their influence⁽⁴⁶⁾ on the plots of "instantaneous copolymer composition" F_1 , against the instantaneous monomer composition in the feed f_1 . Now the ideal copolymer is formed when F_1 is equal to f_1 as represented by the curve (a) of fig.1. This situation is met when there is no preference of the polymer radical to either of the monomers i.e. $K_{11} \cong K_{12}$ and $K_{22} \cong K_{21}$ or $r_1 \cong r_2 \cong 1$. Although the situation is theoretical, the copolymer structure would be completely random. Example of ideal copolymers which are completely random and where the product of the reactivity ratios are approximately unity are copolymers of vinyl acetate and isopropenyl acetate⁽⁴⁷⁾ and tetrafluoroethylene and monochlorotrifluoroethylene.

Regular alternating copolymers will be formed in case where both r_1 and r_2 have close values approaching to zero. Since in this case short sequences of the monomers M_1 and M_2 could tend to form as represented by the curve (V) of Fig. 1. Then the closer the product $r_1 r_2$ is zero, the greater is the tendency for M_1 alternating copolymers are maleic anhydride and styrene⁽⁴⁸⁾ and fumaronitrile and α -methylstyrene⁽⁴⁹⁾. When r_1 and r_2 are both greater than unity i.e., $r_1 \& r_2 \gg 1$, conditions favour to give block copolymers containing long sequences of each monomer. On the other hand when r_1 and r_2 are both less than unity, there is a decided tendency to form an alternating Copolymer. The copolymer composition plot (curve II) contains a point P at which the curve crosses over the diagonal line. At this point, termed the azeotropic copolymerization composition is formed throughout the copolymerization reactions. Example of this type of copolymerization are methacrylonitrile with methylstyrene and acrylonitrile with styrene. Curve (iv) represents a case where $r_1 \gg 1$ and $r_2 \ll 1$. In this case the copolymer consists mostly of monomer M_1 and at high feed composition of M_1 essentially a homopolymer of this monomer is formed. Examples of this type are acrylonitrile with Methylacetate and styrene with vinyl acetate. In the light of above brief discussion it is clear that knowing the value of r_1 and r_2 for a copolymer, some information can be gathered about its structure i.e., about the order of the arrangement of the monomer units in the polymer chain.

1.4. Factors affecting Copolymerization:

Some of the essential factors responsible to affect homopolymerization of monomers are also found effective to influence copolymerization. In the earlier section of this chapter, the influence of temperature, solvents, catalysts and purity of monomers on the homopolymerization of monomers has been described at length. These factors remain also applicable to the copolymerization of monomers but since the process of copolymerization is more complex than the simple homopolymerization of the monomers, some additional factors besides the above have to be given due consideration. Broadly speaking these factors are those which affect directly the reactivity of the monomers and hence their copolymerization. Some important one among these factors are discussed as follows.

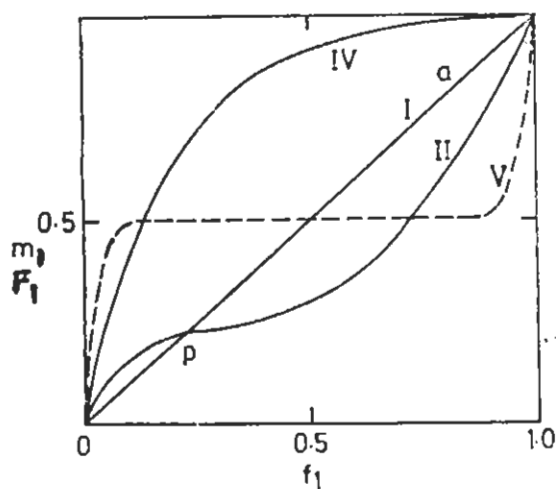


Fig.1.1.

1.4.1. Type of initiation:

As already discussed in the preceding sections that a polymerization reaction can be propagated by the free radical initiation. Copolymerization of monomers is affected to a greater extent by the change of the above types of initiation. For the some reasons, it is seen that even the same pair of monomers often yields a copolymer of differing properties depending upon the type of the initiation employed in the copolymerization reaction. Thus a random copolymer is formed in case of copolymerization of styrene-methyl methacrylate system by the free radical initiation. The same pair of monomers however, by the anionic reaction produces a copolymer which is only rich in one type of monomer i.e., methyl methacrylate. By the cationic reaction, the system can be worked to produce a copolymer which is rich in the other component of the system, i.e., styrene. The change of process to produce the same type of initiation has rather little influence on the reactivity of the monomers. For this reason the results of the free radical initiation by the bulk or the emulsion method would remain comparable to each other. To conclude, it can be said that the reactivity ratios are changed on the copolymerization is greatly influenced as a result of change of the chain carrier.

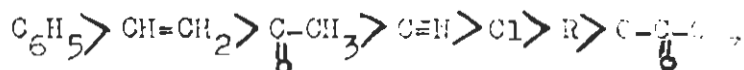
1.4.2. Polar effects:

Polar effects are common in both the ionic and free radical type of copolymerization and influence the reactivity of

the monomers. Electron withdrawing substituents such as COOR, CN, COCH₃, all decrease the electron density of the double bonds in a vinyl monomer while the electron donating groups i.e., CH₃, OR, OCOCH₃ increase the electron density of the double bond. Hence monomers with wide change in polarity undergo copolymerization to give alternating type of copolymers⁽⁵⁰⁻⁵¹⁾.

1.4.3. Resonance stability and steric effects:

Resonance stability inherent in the parent monomers counts their reactivity in the copolymerization process. The character of the neighbouring group in the vicinity of the vinyl bond is important. If the group adds to the delocalization of radical, it would tend to increase the stability of the free radical. Common groups can be arranged with decreasing electron withdrawal capacity as:



Thus styrene radical is strongly stabilized whereas vinyl acetate radical is strongly unstabilized⁽⁵²⁾. Copolymerization of the two monomers requires that stable styrene radical reacts with the unreactive vinyl acetate monomer. This process seems however difficult and hence is very slow to the extent that styrene tends to homopolymerization instead copolymerizing with vinyl acetate.

Both the polar and the resonance effects of monomers can be accounted together in a general scheme from which it would

be possible to predict qualitatively the reactivities of the monomers participating in copolymerization. Such a useful scheme is the Q-e scheme of Alfrey and Price⁽⁵³⁾. In the scheme, the resonance effect of the monomer and their radical are denoted by factors Q, and P respectively while the polar property of the monomers and its radical is denoted by common factor e. The cross propagation reaction rate is correlated by the equation,

$$K_{12} = P_1 Q_2 \exp \{-e_1 e_2\}$$

Where P_1 relates to radical M_1 and Q_2 to monomer M_2 . Similarly the reactivity ratios r_1 and r_2 are related by the relation as given below:

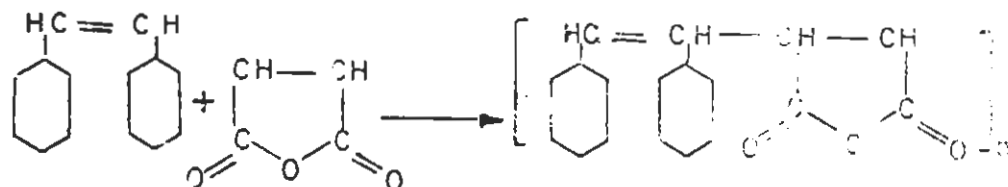
$$r_1 = \frac{K_{11}}{K_{12}} = \frac{Q_1}{Q_2} \exp \{-e_1 (e_1 - e_2)\}$$

$$r_2 = \frac{K_{22}}{K_{21}} = \frac{Q_2}{Q_1} \exp \{-e_2 (e_2 - e_1)\}$$

By choosing arbitrary reference values for styrene of $Q=1.0$ and $e=-0.8$, a table given values of different monomers can be compiled. It would appear that all substituents which conjugate with the double bond have values > 0.5 , while substituents such as Cl, OR and alkyl have values < 0.1 . The e values similarly are different for the electron donating and electron withdrawing groups. Then monomers i.e. maleic anhydride has a value of +1.5 indicating an electropositive double bond. On the other hand monomer i.e., isobutylene has $e=-1.1$. In both cases the

homopolymerization appears to be difficult because of the repulsion of like molecules. It is evident, however, that copolymerization of the oppositely charged monomers would be possible readily.

Although the Q-e scheme is useful to anticipate the reactivity of monomer in a copolymerization reaction, in fact it does not account the steric effects of monomers which are equally important to influence the reactivity of monomer undergoing copolymerization. Steric effects inherent in monomers would inhibit their homopolymerization and similarly tend to inhibit their copolymerization. But some time these effects are overcome and nullified by some other effects. Example to illustrate the same is of monomer e.g., maleic anhydride and stilbene, where the steric effects dominate making the homopolymerization of the individual monomers difficult. Both these monomers get readily copolymerized because the polar effect dominates to overcome the steric effect to yield alternating copolymer as,



1.5. Effect of Organic and inorganic salts and their complexes on Copolymerization of different monomers:

Most olefinic molecules for their polymerisation and copolymerization require some form of activation that may be supplied by thermal photochemical or by the use of a suitable Catalyst. The pure thermal initiation is exhibited by very few monomers such as styrene and methylmethacrylate. Styrene is known to be most active at temperature of 127°C . It shows a thermal self initiation rate of 4% per hour while methylenemethacrylate has an activity of only about 1% that of styrene⁽⁵⁵⁾. In contrast to these studies, vinyl acetate, methyl acrylate and vinyl chloride show no measureable polymerization rate upto a temperature of 100°C . Monomers even in the highly purified state may not polymerize thermally if they are in capable of forming reaction dimer intermediates. Polymerization may also be carried out by using certain organic and inorganic salts and their complexes as a substitute of catalyst. These are discussed individually in more detail as follows:

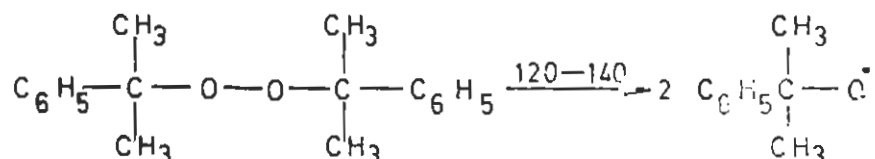
1.5.1. Polymerization using organic catalysts:

Among the most commonly used compounds which are convenient to catalyze the polymerization reaction are all compounds and the peroxides. They are usually molecules of molecular weight between 100-300. These compounds under the condition of reaction slowly

decompose and produce fragments which carry with them an unbonded ligand function or orbitals which react with the π -electrons of a colliding monomer to form covalent sigma bond (56-57).

Out of the important peroxide compounds which are used as catalyst in polymerization are benzoyl peroxides, dicumyl peroxide, acetyl peroxide, t-butyl hydroperoxide, di-t-butyl peroxide etc.

The formation of radical by the thermal decomposition of these peroxides are similar to each other. The dicumyl peroxide decomposes as:

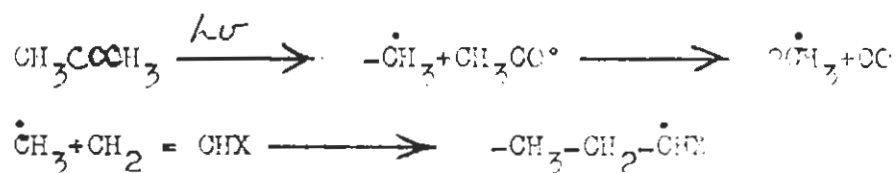


Advantage of the above mentioned compounds is that they cover fair temperature range and are easy to handle. These advantages, however, a serious drawback in the use of these compounds i.e., peroxidic compounds is that they possess oxidizing character and hence show corrosive action. Also the formation of undesirable product takes place simultaneously in some instance during their reaction with monomers (58-67). It is therefore of considerable interest to find some alternatives which are free from these defects. Azo-compounds such as 2-2'-azobis(methyl isobutyrate) were found to be a good replacement in some cases over the peroxidic

compounds. Like the latter these compounds also decompose with the formation of free radicals and nitrogen is liberated on decomposition accordingly as follows:



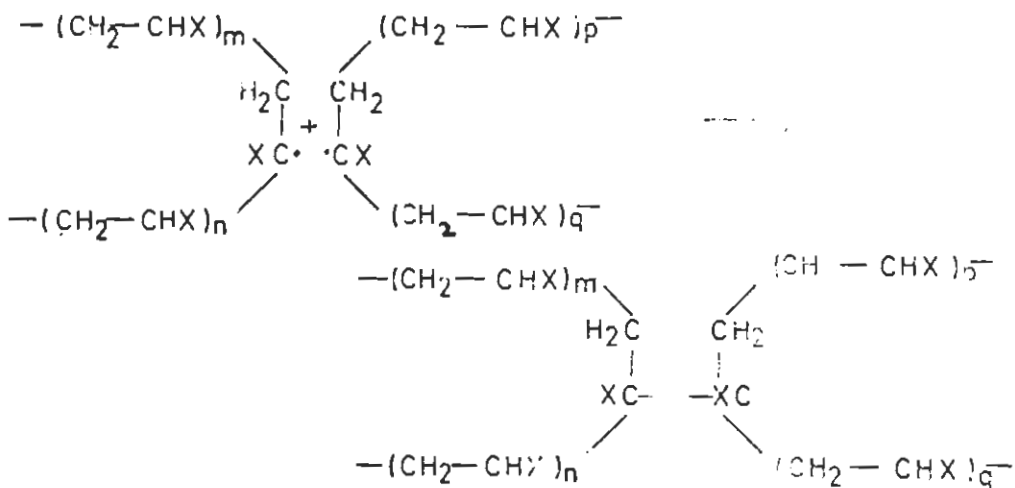
Some organic compounds although themselves do not behave as catalysts in polymerization reaction, their presence with the monomer enhance and facilitate polymerization. Typical examples of such compounds are of the photoinitiators which include compounds such as acetone⁽⁶⁸⁾ benzil⁽⁶⁹⁾ and benzoin⁽⁷⁰⁾ etc. etc. Usually these compounds decompose with the absorption of U.V. rays to produce radicals which initiate the growth of polymeric radical in monomer by undergoing reaction involving the olefinic bond e.g.,



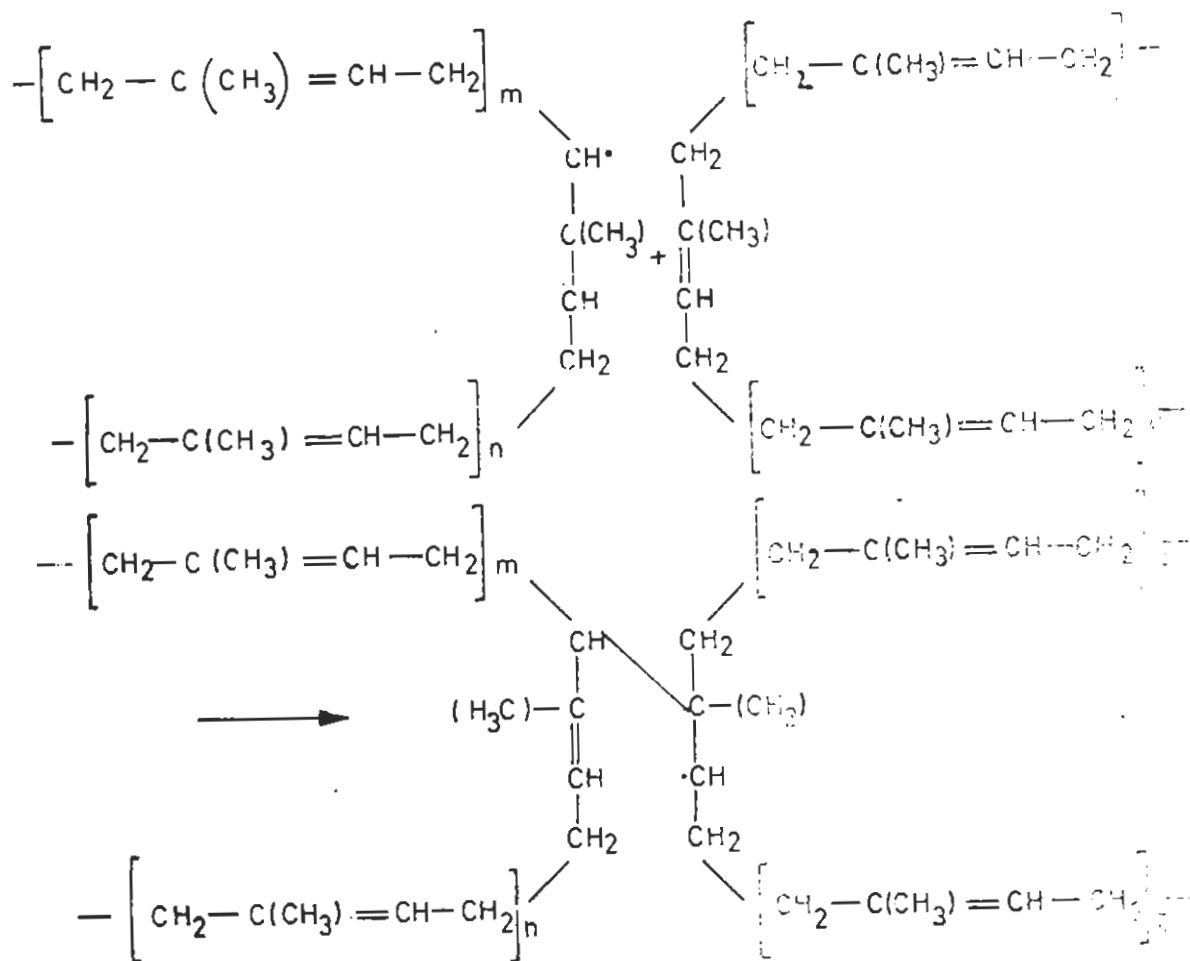
Organic vatdyes such as fluorescein, trypanblue and chlorophyll also catalyse polymerization in a similar way and are useful sensitizer to polymerise styrene⁽⁷¹⁾ and methyl methacrylate⁽⁷²⁾. The mode of their reaction involves a similar type of mechanism as mentioned above.,

The organic compounds acting as catalyst in polymerization reaction besides their application as photosensitizer etc. find

also extensive application in crosslinking polymer to enhance their mechanical properties. Of course without the introduction of thermal stability and important properties such as elasticity, tensile strengths and rigidity. This can be illustrated by the sample of e.g., rubbers of the diene types. These polydienes can not be extended to any desired length and would break by an applied force with the introduction of crosslinkages in the system the extension to any desired length of the material would be possible. The mechanism of crosslinking polymer by these organic compounds remain again the same e.g., attack on the monomer by the radical formed by the decomposition of the catalyst. Polymeric radicals are produced by abstraction of hydrogen from the monomer. Crosslinking occurs when two radicals combine in the following manner⁽⁷³⁾.



In diens, crosslinking occurs much more readily than the vinyl type of polymerization because of the presence of adjacent double bond e.g. (74),



Crosslinked polymers do not dissolve but merely swell. These polymers have no softening zone corresponding to those of the linear polymers. If the crosslinking density is sufficiently high reactivity of the polymers eventually disappear and hence gives rise a rigid and stable net work.

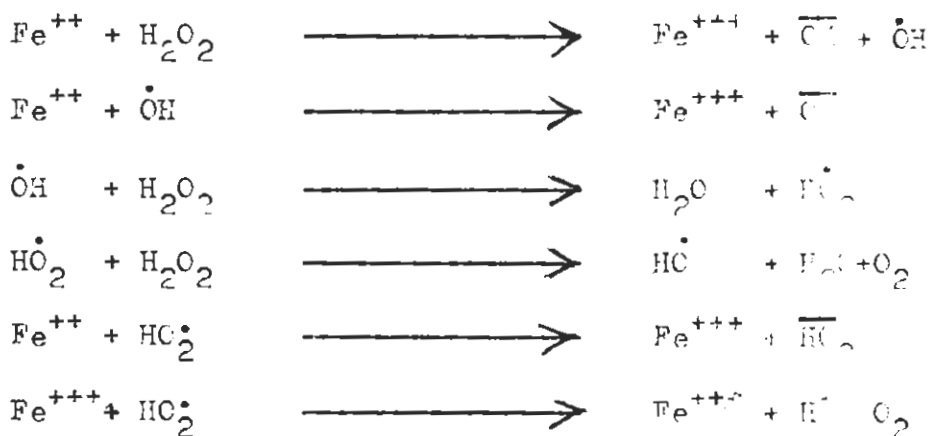
1.6. Use of Organo-inorganic Compounds as Catalysts in Polymerization of monomers:

Like the Organic Compounds as mentioned above some inorganic as well as organo-inorganic Compounds also initiate or help in initiating the polymerization of various Compounds. Important ones among the list of such compounds are potassium per sulphate, metal alkyls, Friedel Crafts Catalysts, Ziegler-Natta Catalysts. These compounds take part in polymerization reactions both through free radical and by ionic mechanism discussed bellow.

1.6.1. Redox Catalysts:

In a series of earlier papers, (75-77) it has been reported that the addition of small amount of reducing agents enhances further, the activity of the peroxide Catalysts in the aqueous polymerization of monomers. The term "reduction activation" polymerization has been coined for this effect and the most complete and thorough study of it was made by F.C. Mayo and collaborators. (78-84) They have reported the effect of ferrous

ions on the aqueous polymerization of acrylonitrile, methylmethacrylate, methacrylic acid, methyl acrylate and styrene by using H_2O_2 as initiator. The system gave rise to a much more rapid formation of polymer than by the use of H_2O_2 alone. In the absence of monomer, the peroxide decomposed according to the Haber-Weise mechanism with evolution of oxygen,



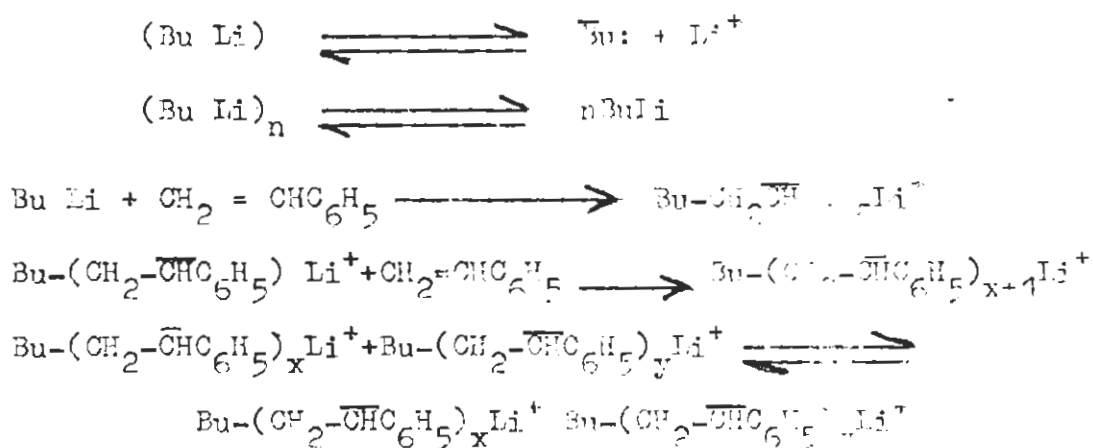
In the presence of a monomer however the Oxygen production was very much reduced or even stopped owing to reaction of the monomers molecule with the chain carriers,



The use of potassium persulphate in combination with reducing agents such as argentous or ferrous salts, hydrazine, hydrogen sulphide and thiosulphate is also common in a box system⁽⁸⁵⁾. Mercaptans have also been reported as suitable reducing agents for use with persulphate⁽⁸⁶⁻⁸⁷⁾.

1.6.2. Metalalkyls:

In the category of organo metallic compounds the organo alkali metal compounds are especially the most reactive reagents e.g. in initiating polymerization of the olefinic monomers (88). Illustration will be made by taking into consideration of butyl lithium as a representative of organo alkali metal compounds. It dissociates in organic liquid into Li^+ and Bu^- ions. The butyl carbanion attack itself to the double bond of the monomer as follows (89-90)



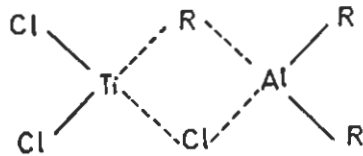
The other metal alkyls which are in use for polymerization of olefinic monomers are $\text{Be}(\text{C}_2\text{H}_5)_2$, $(\text{C}_2\text{H}_5)_2\text{Zn}$, $(\text{C}_2\text{H}_5)_2\text{Mg}$, Br , $\text{Cd}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{AlCl}$ and $\text{Ph}(\text{C}_2\text{H}_5)_4$. On the one hand these alkyls are important to form polymer of high molecular weight. They are of vital use of on the other hand because they keep stereoregularity of the polymer chain. More particular to mention

in this regards are the transition metal halides such as $TiCl_4$, $TiCl_3$, VCl_4 , $CuCl$, $AgCl$, $CrCl_3$, and $AlCl_3$ for their specific use as catalysts to form stereoregular polymers. The above mentioned metal alkyls in combination with transition metal halides or esters give rise to the formation of active initiators known with the general name ziegler-Natta Catalysts. (91-97)

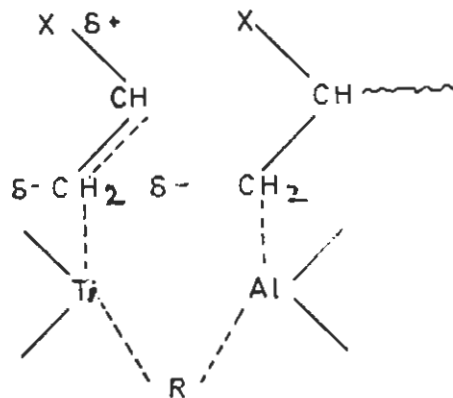
Two features can be controlled with the help of these catalysts (a) the rate and (b) the specificity of the reaction but unfortunately much depends upon the nature of monomer involved in the reaction and hence only a selective trial limits control over both of these aspects. The propagation taking place at a carbon to transition metal bond, this active centre being anionic in character. This system is deprived of free radical reactions since chain transfer and catalyst consumption does not take place. The active centres live longer than radicals and hence behave like a living polymer systems where block copolymers can be produced by alternate feeding of two monomers. From the various reaction mechanism suggested so far, a common view is that active centres are localised rather than migrating and α -olefin is complexed to the transition metal centre prior to incorporation into the chain i.e., growth is always from the metal end of the growing chain. The active species can be then either be monometallic or bimetallic (91-95).

Natta and his associates proposed a mechanism in which active centre is formed by the chemisorption of an electropositive metal

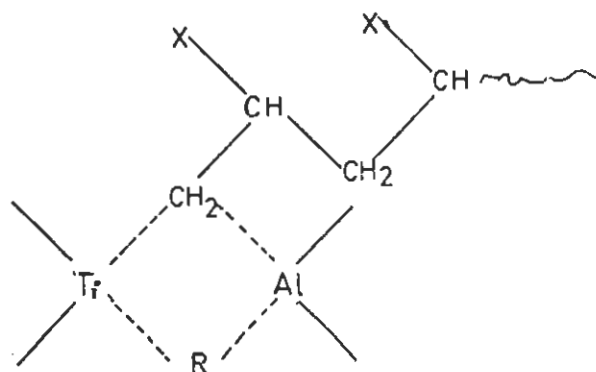
metal alkyls, on the co-catalyst surface yielding an electron deficient complex⁽⁹⁶⁾.



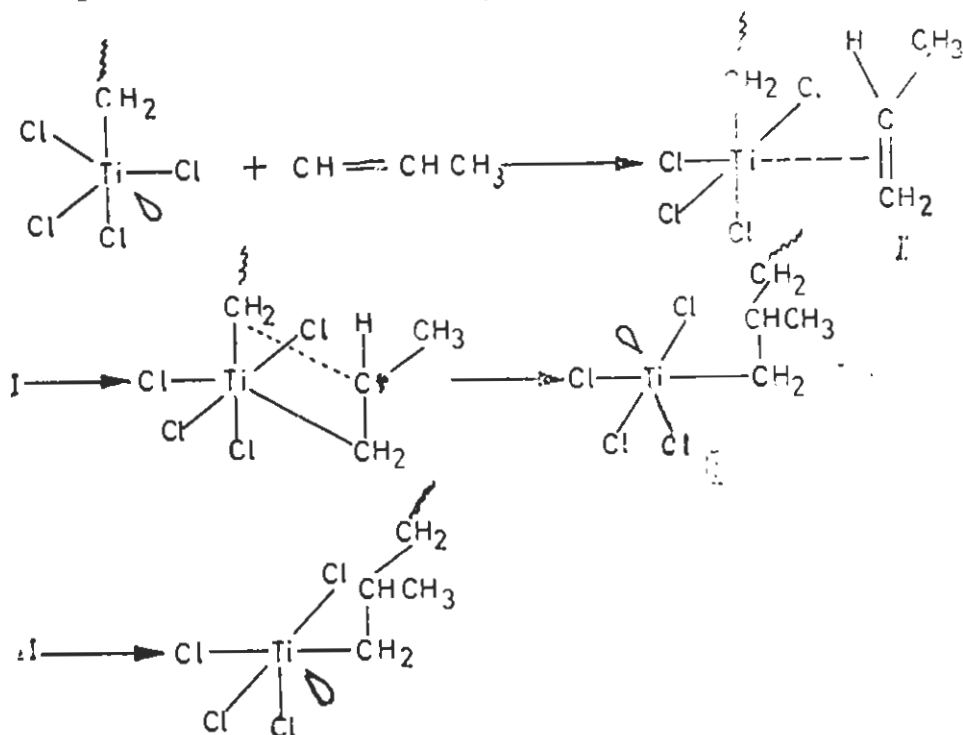
Following the partial ionization of the alkyl bridge, the nucleophilic olefin forms a π -complex with the ion of the transition metal and the monomer is included in a six membered ring transition state.



The monomer is then incorporated into the growing chain between the Al and C allowing the regeneration of the complex,



The majority of workers⁽⁹⁷⁻⁹⁹⁾ believed however that d-orbitals in the transition elements are the main reasons for the catalytic activity and that chain growth occurs at the titanium-alkyl bond. The attacking monomer essentially non polar forms a complex with the titanium,



Three essential points involved in the above mechanism are given as under,

- (1) Ti^{3+} ion has an octahedral valency and hence form complex with the monomer. (2) it predicts an alkyl to transition metal bond. and
- (3) the growing polymer chain is always attached to the transition metals.

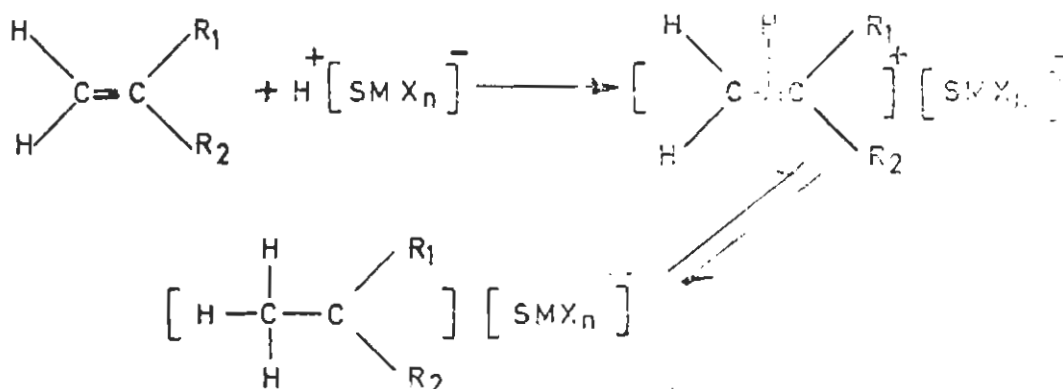
1.7. Olefin polymerization in presence of inorganic salts:

Since the last few years attempts have been made to find the effect of inorganic salts on the polymerization of monomers. The previous workers show that the pure inorganic salts such as $ZnCl_2$, $AlCl_3$, BCl_3 , $TiCl_4$, $SnCl_4$, $FeCl_3$, $CdCl_2$, $ZrCl_4$, UCl_4 etc. have a definite influence on the rate of polymerization of monomers. The Lewis acids Mx_n often named as Friedel-Crafts Catalysts i.e., $AlCl_3$, BF_3 , $TiCl_4$, $SnCl_4$ take part in the polymerization process of the monomers but usually they are not themselves alone particularly active to act as initiator. They gain activity in combination with the Co-catalyst SH to act as a proton donor.

The general mode of reaction may be represented by the following equation,



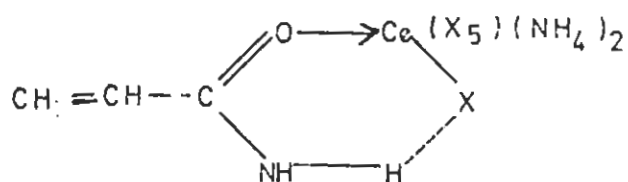
The probable steps in initiating polymerization are:



It would be clear from the above that the mechanism has total similarity with the Cationic type of initiating polymerization proceeding through the formation of carbonium ion. Proton is added to the double by the reaction of the π -electron forming a complex in the first step. The second step is simply a slow intermolecular exchange reaction.

A more recent study in the polymerization of monomers such as methyl acrylate, 4-vinyl pyridine vinyl carbazole and acrylonitrile also show that some ceric salt are also capable to initiate polymerization of the above mentioned monomers ⁽¹⁰⁷⁾.

It is reasonable to assume that these salts coordinate with monomer such as acrylamide,



Overall more interesting is the fact that the ceric salt i.e., ZnCl_2 , AlCl_3 , SnCl_4 and AlBr_3 etc. enhances the rate of free radical homopolymerization, copolymerization and terpolymerization of vinyl monomers particularly containing conjugative nitrile and carbonyl groups ⁽¹⁰⁸⁻¹¹⁷⁾. The enhancement has been attributed due to complex formation between, the salt and the monomer giving rise to an increase in the delocalization of

electrons in the complex monomer compared to the free monomer,



1.8. Aim and Object

The majority of vinyl and allyl polymers are prepared with the aid of catalysts which can initiate and propagate chain reactions in monomers through free radical mechanism, where the olefinic double bond undergoes simple addition reaction through polar or ionic mechanism. Such catalysts are the group of stable compounds e.g., organic peroxides, azocompounds, diazothioethers etc. Besides these compounds, some purely inorganic compounds are also known to initiate or help in initiating the olefinic polymerization reactions. They include Lewis acids, Ziegler-Natta catalysts, Friedel-Crafts catalysts and metal alkyls. All these catalysts have brought a tremendous change in the field of polymer chemistry and produce polymers of regular structure and can be carried out at low temperatures. Most of these catalysts are not active alone and they require some co-catalyst which help in producing active species for initiating the reaction.

A number of workers have been searching for the new initiation systems of radical reactions based on metallic complexes. Recently they chelate complexes of transition metals opened a new field of initiating vinyl and allyl polymerization. In this respect such initiation system might be of interest which generate free radicals by chelate interaction with another component of the initiation system. Here also the chelate itself and other component of the

initiation system do not necessary act as effective initiator for radical reactions when they are used independently. Besides the metallic complexes the purely inorganic salts like ZnCl_2 , LiCl , AlCl_3 etc. are successfully been used in enhancing the free radical polymerization of vinyl and allyl monomers initiated by organic peroxides and azo-compounds. But the survey of the literature also provides evidences that thermally initiated polymerization and copolymerization of vinyl and allyl monomers occur spontaneously in the presence of ZnCl_2 without the addition of any radical initiator. The mechanism covering the kinetic details of this type of radical polymerization and copolymerization has not yet been studied thoroughly.

The use of all above mentioned catalysts ~~or~~ pair of catalysts involve many complications like availability, preparation of organic catalysts, co-catalysts and metallic complexes and their physicochemical studies etc. These complications may only be removed by selecting such an initiation system which are free ^{from} these involvements.

Therefore this work was carried out to overcome the above mentioned complications and to select a simple initiating system. The simple initiating system may be like the use of inorganic salts together with zinc chloride. These salts do not involve any preparation and are economical and may be used alone for polymerization reactions. It is observed that like ZnCl_2 , other inorganic salts form complexes with acrylonitrile, allyl alcohol, methyl

acrylate and methylmethacrylate depending upon the solubility of inorganic salts in the monomers. But those salts which do not form complexes and are not soluble in the monomer may decrease or increase the rate of thermally initiated polymerization. It may be perhaps due to the adsorption of the reacting monomers on the solid surface of inorganic salt. The cracks and imperfections of the crystals of catalysts act as the active centers to release the radicals. For this purpose, the effects of inorganic salts were studied on the monomer reactivity ratios, molecular weight and some other physical properties of copolymers. The systems selected for the study are:

Styrene-acrylonitrile

Acrylonitrile-allyl alcohol

Styrene-allyl alcohol

Styrene-methyl acrylate

Styrene-methylmethacrylate and

Acrylonitrile-vinylidene chloride

Two types of inorganic salts are selected. Some of them are soluble in the monomers and some of them are insoluble. The inorganic salts selected are copper chloride, cobalt chloride, strontium chloride, mercury chloride, cadmium chloride, cerium chloride, zinc chloride, platinum chloride, nickel chloride and chromium chloride.