CHAPTER 1

INTRODUCTION
1.1 General Introduction

During the past few decades macromolecular science has witnessed a spectacular growth in the development of its various processes and the understanding of its principles. Many a new type of polymer has been synthesised and new facts have opened up with the systematic research in this field. The present trend of research in polymers is thus oriented towards the synthesis of new types of monomers and polymers, their characterisations and applications in newer fields.

Macromolecules or high polymers are the results of a systematic process of knitting up of small molecules through primary valence forces following the basic principles of classical chemistry. One important area of this broad field is concerned with the addition type of polymerisation of small vinyl compounds capable of undergoing such reactions. Two major influences are operative in progressing these reactions and they are either ionic or radical in nature. Three major steps are encountered in such reactions and very often a fourth step is also associated. These are termed as initiation, propagation and termination steps and the latter one as chain transfer. During this process, the vinyl compound (termed as monomer) is first activated through its reactive site by heat, light, catalyst or similar activating agents which in turn rapidly joins other monomer molecules to form relatively bigger chains and ultimately these chains loses their activity and stop growing. Whereas the potentiality of any monomer molecule to undergo such types of polymerisation
reactions are determined by the thermodynamic factors, the relative rate with which all these reactions occur is governed by the kinetic laws.

1.2 Kinetic Studies

One of the most important methods for studying the mechanism of polymerisation is the study of the kinetics of the process under different conditions. The kinetic method is extremely valuable because it yields quantitative relationships between the individual elementary reactions and the observed overall reactions. Such relationships are established from the empirically found kinetic relationships with the theoretical equations deduced on the assumption that a given complex of elementary reactions involved in the process. Moreover, kinetic investigations also yield the kinetic constant of individual elementary reactions, which makes it possible to study the quantitative dependence between the chemical structure of the molecules and their reactivity when participating in certain given reactions. It is thus of much interest to review the kinetic scheme operating for a typical free radical initiated vinyl polymerisation.

1.3 Kinetic Scheme

The traditional kinetic scheme for radical polymerisation in which chain reaction is initiated by the thermal or photochemical decomposition of a suitable molecule, I, takes into account three consecutive reactions: initiation, propagation, and termination.
plus, if chain transfer is possible, several competing reactions. Thus,

Initiation:

\[ \begin{align*}
    & I \xrightarrow{k_d} 2R^* \\
    & R^* + M \xrightarrow{k_i} P_1
\end{align*} \]

\[ \begin{align*}
    & \frac{d[R^*]}{dt} = R_1 = 2k_d [I] \\
    & -\frac{d[R^*]}{dt} = k_i[R^*][M]
\end{align*} \]

Propagation:

\[ P_1^* + M \xrightarrow{k_p} P_{1+1} \]

Transfer:

\[ \begin{align*}
    & P_1^* + S \xrightarrow{k_s} P_1 + S^* \\
    & S^* + M \rightarrow P_1
\end{align*} \]

Termination:

\[ \begin{align*}
    & P_1^* + P_s \xrightarrow{k_t} \text{Polymer} \\
    & -\frac{d[P^*]}{dt} = 2k_t [P^*]^2
\end{align*} \]

where \([M]\) and \([R^*]\), and \([P^*] = \sum [P_n]\) are the concentrations of monomer and primary radicals, and the total concentration of polymer radicals, respectively. \(S\) represents a chain transfer agent which may be the monomer, initiator, polymerisation solvent, or another molecule present in the system. Assuming radical reactivity is
independent of radical size and any transfer derived radicals, \( S' \), rapidly add monomer and are not consumed in any other process, application of the stationary state hypothesis leads to the following expression for the concentration of polymer radicals.

\[
\left[ P \right] = \left( \frac{R_I}{2k_t} \right)^{\frac{1}{2}} = \left( \frac{k_d[I]}{k_t} \right)^{\frac{1}{2}}
\]  \hspace{1cm} (1)

Providing the kinetic chain length is large and transfer to monomer not very efficient, the rate of polymerisation is given by

\[
R_p = - \frac{d[\text{M}]}{dt} = k_p [\text{M}] [P]
\]  \hspace{1cm} (2)

and hence

\[
R_p = k_p [\text{M}] \left( \frac{k_d[I]}{k_t} \right)^{\frac{1}{2}}
\]  \hspace{1cm} (3)

Sometimes this equation is modified to

\[
R_p = k_p [\text{M}] \left( \frac{k_d[I]}{f k_t} \right)^{\frac{1}{2}}
\]  \hspace{1cm} (4)

where 'f' is an initiation efficiency factor introduced to allow for the probability that not all primary radicals produced attack monomer. Thus efficiencies of less than 100% can be caused in two ways: the initiator may, in part, decompose by a mechanism which does not produce radicals capable of initiating polymerisation, or, alternatively, some of the radicals may not initiate reaction chains but instead engage in other reactions. The wastage reactions might be:
(a) a direct interaction of radicals derived from the initiator

(b) a termination process involving a polymer radical and an initiator radical i.e. primary radical termination

(c) reaction of the radical with another component of the system.

'f' is often assumed to be independent of $[M]$ and $[I]$. According to Eqn.(3), the monomer and initiation rate exponents should be 1 and 0.5 respectively. The kinetic scheme also predicts that any chain transfer should not affect the rate of polymerisation although, of course, it will significantly alter the mol.wt. of the polymer formed. If primary radicals are generated photochemically and assuming negligible light absorption occurs in the system, the rate of photoinduced autopolymerisation is given by:

$$R_p = k_p \left( \frac{f k I_o}{k_t} \right)^{\frac{1}{2}} [M]^{3/2} \quad \ldots \quad (5)$$

In case of photopolymerisation induced by a photosensitiser, the rate of polymerisation can be expressed as

$$R_p = k_p \left( \frac{f k I_o [P]}{k_t} \right)^{\frac{1}{2}} [M] \quad \ldots \quad (6)$$

The rate of thermoinitiated polymerisation may be expressed as.
This equation is subject to variations because the mechanism of thermoinitiation appears to vary.

Two other parameters which are related to the rate equation are of interest: the degree of polymerisation and the energy of activation. If chain transfer is absent, the degree of polymerisation will depend upon the average number of monomer units which add to an active site before termination (the kinetic chain length, $\gamma$) and upon the method of termination. The kinetic chain length is the ratio of the rate of propagation to the rate of initiation, or assuming steady-state conditions, to the rate of termination:

$$\gamma = \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad ... (8)$$

If termination occurs by disproportionation, the kinetic chain length is equal to the number average degree of polymerisation ($\overline{DP}$); if termination takes place by coupling, $\overline{DP} = 2 \gamma$. From these equations it can be seen that $\overline{DP}$ will be directly proportional to the monomer concentration, but will be inversely proportional to the square root of $[I]$. For thermoinitiated polymerisations, $\overline{DP}$ is independent of concentrations.

The energy of activation for polymerisation is determined from the rate constants at several different temperatures by means of
the Arrhenius equation. Because the reaction rate which is being measured is not a single reaction rate but the sum of the rates of three consecutive reactions, the activation energy which is measured from the sum of the rate constants, is a sum of the activation energies of the three component reactions. Eqn.(3) shows that the rate constant for polymerisation is equal to \( k_p(k_d/k_t)^{1/2} \); therefore,

\[
E_a = \frac{1}{2} E_d + (E_p - \frac{1}{2} E_k) \quad \text{... (9)}
\]

The quantity \( E_p - \frac{1}{2} E_k \) reflects the energy required to polymerise a given monomer. The activation energy for the decomposition of the initiator, \( E_d \), like the rate of dissociation, \( k_d \), depends solely upon the initiator.

1.4 Chain Transfer

The chain transfer reaction may be depicted as

\[
\begin{align*}
    -\text{M}^* + \text{XA} & \quad \xrightarrow{k_{tr}} 
    \quad -\text{M} - \text{X} + \text{A}^*
\end{align*}
\]

where \(-\text{M}^*\) is the growing polymer chain and \(\text{XA}\) may be monomer, initiator, or any other substance and \(\text{X}\) is the atom or species transferred. The rate of chain transfer is given by

\[
R_{tr} = k_{tr}[-\text{M}^*] [\text{XA}]
\]

where \(k_{tr}\) is the rate constant for the chain transfer reaction.

Chain transfer results in the formation of a new radical \(\text{A}^*\) which
then re-initiates polymerization.

$$A^* + M \xrightarrow{k_a} M^*$$

Chain transfer usually leads to a lowering of $\bar{P}_n$. The effect of chain transfer on $R_p$ is not evident but is dependent on whether the rate of monomer addition to the new radical $A^*$ is comparable to that of the normal propagating reaction. The four main situations that may be encountered are presented in Table 1 below.

**Table 1**

<table>
<thead>
<tr>
<th>Case</th>
<th>Relative rate constants for transfer reaction, propagation and reinitiation</th>
<th>Type of effect</th>
<th>Effect on $R_p$</th>
<th>Effect on $\bar{P}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$k_p \gg k_{tr}$ $k_a \sim k_p$</td>
<td>Normal chain transfer</td>
<td>None</td>
<td>Decrease</td>
</tr>
<tr>
<td>2</td>
<td>$k_p \ll k_{tr}$ $k_a \sim k_p$</td>
<td>Telomerization</td>
<td>None</td>
<td>Large decrease</td>
</tr>
<tr>
<td>3</td>
<td>$k_p \gg k_{tr}$ $k_a \ll k_p$</td>
<td>Retardation</td>
<td>Decrease</td>
<td>Decrease</td>
</tr>
<tr>
<td>4</td>
<td>$k_p \ll k_{tr}$ $k_a \ll k_p$</td>
<td>Degradative chain transfer</td>
<td>Large decrease</td>
<td>Large decrease</td>
</tr>
</tbody>
</table>

For chain transfer in case 1, the kinetic chain length remains unaltered but the number of polymer molecules produced per kinetic chain length is altered. The number average degree of polymerization $\bar{P}_n$ is no longer given by $\gamma$ or $2 \gamma$ for disproportionation and coupling respectively. In the polymerization process, the molecular
weight of the polymer formed may be controlled at a specified level using controlled chain transfer process.

The degree of polymerization can now be redefined as the rate of polymerization divided by the sum of all rates of chain ending process (i.e., the normal termination mode plus all chain transfer reactions). For the general case of polymerization initiated by the thermal homolysis of an initiator, involving termination by coupling and chain transfer (to monomer, initiator and solvents), the number average degree of polymerization is given by,

\[ \bar{P}_n = \frac{R_p}{(R_t/2) + k_{tr,M} [M]^2 + k_{tr,S} [S]^2 + k_{tr,I} [I]^2} \]  \hspace{1cm} (10)

The first term in the denominator denotes rate of formation of pairs of chain ends through termination by coupling and the other three terms denote rate of formation of pairs of chain ends through chain transfer by monomer, solvent and initiator respectively. A chain transfer constant \( C \) for a substance is defined as the ratio of rate constant \( k_{tr} \) for the chain transfer reaction to the rate constant \( k_p \) for the propagation reaction. The chain transfer constants for monomer \( C_M \), solvents \( C_S \) and initiator \( C_I \) may then be given by,

\[ C_M = \frac{k_{tr,M}}{k_p}, \quad C_S = \frac{k_{tr,S}}{k_p}, \quad C_I = \frac{k_{tr,I}}{k_p} \]  \hspace{1cm} (11)

Thus combining equations (2), (4), (10) and (11), we get
The above equation, commonly known as Mayo equation shows the quantitative effect of the various chain transfer reactions on the number average degree of polymerization.

1.4a Transfer to solvents or other additives

In presence of solvents or any other added substance with which the radical chain may get involved in transfer reactions, the third term of the general Eqn. (12) usually makes a major contribution to the determination of the degree of polymerization. Using low [Initiator] or initiator with negligible C_I value the last term of the Eqn. (12) may be taken as negligible. The first term may be kept constant by so adjusting Initiator as to keep \( \frac{R_p}{[M]^2} \) constant while \([S]\) is varied. Thus, equation (12) reduces to

\[
\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_{n0}} + C_S \frac{[S]}{[M]} \quad \ldots \quad (13)
\]

where \( \bar{P}_{n0} \) is the average degree of polymerization obtained in absence of the solvent. Now C_S can be determined from the slope of the plot of \( \frac{1}{\bar{P}_n} \) vs \( \frac{[S]}{[M]} \).

1.5 Deviations in Normal Kinetics

Although the above kinetic relationships have been shown to hold in a number of cases, in a large number they are not observed.
Deviation from the expected monomer exponent are more common, numerous values greater or less than unity have been reported. In some cases the monomer order varies with monomer concentration. Initiator and intensity exponents different to 0.5 are less common but values below this figure have been reported in the polymerisation of MMA and higher methacrylate and acrylate esters, values greater than 0.5 have also been observed, particularly in polymerisations taken to high conversions.

Several mechanisms have been advanced to account for these anomalies and they involve modification of the initiation, termination propagation steps of the above chain mechanism. Modification of the initiation or termination mechanism clearly leads to a different expression for the concentration of polymer radicals and hence rate of polymerisation (Eqns.1 and 3) although Eqn.(2) still applies. In contrast, kinetic schemes involving more complex propagation processes lead to different expressions to Eqn.(2) for the rate of polymerisation although Eqn.(1) remains valid.

1.5a Initiation Step

Cage Effect: To account for a deviation in monomer exponent from 1 to 1.5 in dilute solution for the polymerisation of styrene in toluene solution, initiated by peroxide, Schulz suggested a variation in the efficiency of initiation with monomer concentration. He postulated that a complex was formed between monomer and initiator,

\[ M + I \xrightarrow{\text{Complex}} 2R^* \]
and that the unimolecular decomposition of the complex was the true source of the primary or initiating radicals. Matheson suggested the results can be better explained in terms of a physical phenomenon known as "radical caging". This theory recognises that primary radical pairs, formed by the decomposition of an initiator molecule, are surrounded by a "cage" of solvent and monomer molecules. Consequently they may undergo many mutual collisions before one of the radicals escapes from the cage either by diffusion or reacting with monomer molecule constituting the "cage wall". Recombination of geminate radicals within the cage is thus a distinct possibility. The following kinetic scheme summarises these processes where \((2R^*)\) represents a "caged" radical pair and \(R^*\) and \(P_1^*\) are "free" primary radicals and polymer radicals, respectively.

\[
\begin{align*}
1. \quad & I \xrightarrow{k_1} (2R^*) \\
2. \quad & (2R^*) \quad \xrightarrow{k_2} Q \quad \text{Recombination} \\
3. \quad & (2R^*) + M \xrightarrow{k_3} P_1^* + R^* \\
4. \quad & (2R^*) \xrightarrow{k_4} 2R^* \quad \text{Diffusion}
\end{align*}
\]

Free primary radicals can initiate polymerisation in the normal way and propagation and termination reaction then proceed as in the simple polymerisation scheme. If radicals mainly escape from the cage of reaction with the nearest monomer molecule i.e. \(k_3[M] \gg k_4\), the processes 2 and 3 are in direct competition. Under these conditions the efficiency of initiation clearly depends on the \(\ldots\)
monomer concentration and it can be shown that

\[
R_p = \frac{k_p [M] k_{1/2} [I]^{1/2}}{k_t^{1/2}} \frac{k_3 [M]}{k_2 + k_3[M]} \quad \quad \cdots (14)
\]

The results obtained by Schulz are thus accounted for by the radical caging theory. In terms of Eqn. (4), the effect of primary radical caging will be to make 'f' monomer dependent. It is interesting to note that radical recombination within a solvent cage is a first-order process, so that the initiator rate exponent remains as 0.5.

1.5b Termination Step

1) Primary radical termination: Bamford et al studied the thermal-initiated polymerisation of styren in DMF solution. To explain the kinetic results obtained, the authors postulated a termination mechanism in which primary radicals were involved. Thus in addition to the single termination reaction given above, the following additional processes were assumed to occur:

\[
P_T^* + R^* \xrightarrow{k_t^*} \text{polymer} \quad - \frac{d [P^*]}{dt} = k_t [R^*] [P^*]
\]

\[
R^* + R^* \xrightarrow{k_t^*} \text{products} \quad - \frac{d [R^*]}{dt} = 2k_t [R^*]^2
\]

By assuming a geometrical mean relationship between the termination coefficients, that is \( k_t^* = 2(k_{t1} k_{t2})^{1/2} \), the following equation was derived at constant monomer concentrations:

\[
\]
where $K_1$ and $K_2$ are constants. The experimental results fitted this equation.

Allen and Patrick later pointed out that since $k_1$, $k_2$ and $k_j$ are diffusion-controlled constants, a geometric mean relationship is not valid and an arithmetical mean relationship should apply. Thus when the rate constants are defined as in the scheme above, $k'_t = (k_t + k_j)$. They also showed that deviations in Eqn.(3) due to primary radical termination can be expected when relatively low values of either $k_1$, $k_t$ or $[M]$ apply, especially if the rate of initiation is high.

ii) Degradative chain transfer: Burnett and Loan studied the polymerisation of MMA, Methyl Acrylate and Vinyl Acetate in benzene solution. Anomalous, high monomer exponents were found with the latter two monomers. To explain these, it was proposed that the radical produced by transfer to solvent was capable of reacting with a growing polymer chain, thereby bringing about cessation of growth. In this mechanism, called degradative chain transfer, the additional termination reaction

$P_r^* + S^* \rightarrow \text{polymer}$

$2S^* \rightarrow \text{product}$

are included in the simple polymerisation scheme, where $S$ and $S^*$ in
\[ R_p = \left[M\right]^2 R_1 \left[ K_1 [M]^2 + K_2 C [M] [S] + K_3 C^2 [S]^2 \right]^{\frac{1}{2}} \]  \quad \ldots (16)

where \( C \) is the Mayo transfer constant \( (= k_s/k_p) \) and \( K_1, K_2 \), and \( K_3 \) are composite constants involving rate constants for propagation and termination reactions, including those involving solvent radicals. The above mechanism successfully accounts for high monomer orders, since on dilution the overall rate of termination increases due to the increasing importance of reactions involving solvent radicals. At the same time the initiator exponent should become greater than 0.5. Atkinson et al have shown in a recent publication that under certain condition an initiator exponent 0.5 may in fact result from a mechanism involving degradative chain transfer to solvent. In this case a plot of \( [M]^2/R_p^2 \) vs \( [S]/[M] \) should be linear.

Park and Smith have derived a general equation which predicts the monomer and orders shown in Table 2 for degradative chain transfer processes occurring with monomer, initiator and solvent.

<table>
<thead>
<tr>
<th>Transfer agent</th>
<th>Order in Monomer</th>
<th>Order in Initiator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>0 - 1.0</td>
<td>0.5 - 1.0</td>
</tr>
<tr>
<td>Initiator</td>
<td>\geq 1.0</td>
<td>0 - 0.5</td>
</tr>
<tr>
<td>Solvent</td>
<td>\geq 1.0</td>
<td>0.5 - 1.0</td>
</tr>
</tbody>
</table>

This case represent solvent and solvent derived radical, respectively. Making the usual assumption regarding stationary state and length of chains, Burnett and Loan derived the following equation
An alternative mechanism involving degradative chain transfer has been considered by Scott and Senogles. This involves a postulated intramolecular transfer processes which produces a polymer radical of reduced propagation reactivity. Processing involving the establishment of a six-membered ring transition state are more likely to be favoured. Similar types of "backbiting" reaction is well known in the polymerisation of ethylene and there is evidence for related reactions in vinyl acetate polymerisation. Applying the usual stationary state assumptions and assuming intramolecular transfer is not a frequent process, the following expression has been derived:

\[ R_p = \frac{k_p[M]}{(2k_t)^{\frac{1}{2}}} \left[ \frac{R_1^{\frac{1}{2}}(2k_t)^{\frac{1}{2}} + k_p[M]}{k_s + k_p[M] + 2k_t^{\frac{1}{2}} R_1^{\frac{1}{2}}} \right] \] ... (17)

This equation can account for monomer and initiator orders greater than 1 and 0.5 respectively. Furthermore the effect will be independent of the chemical nature of the solvent. In some circumstances \( k_p[M] \) and \( k_s \) may be significantly greater than \( R_1^{\frac{1}{2}}(2k_t)^{\frac{1}{2}} \), so that the above equation reduces to

\[ R_p = \frac{k_p[M]}{(2k_t)^{\frac{1}{2}}} \left[ \frac{k_p'[M]}{k_s + k_p'[M]} \right] \] ... (18)

This equation predicts a normal initiation exponent, although a high monomer order would still apply.
iii) Diffusion effects:

It is now generally assumed that the termination step in vinyl polymerisation is diffusion controlled under most conditions. North has proposed a three-stage termination process in which polymer molecules first approach each other so that certain segments are in contact (translational diffusion). Rearrangement of the polymer chains (segmental diffusion) can then occur so that the two radical chain ends approach sufficiently close for the third step, chemical reaction, to take place.

1. \[ R^- + R^- \xrightarrow{17} [R^- \ldots R^-] \]

2. \[ [R^- \ldots R^-] \xrightarrow{1} [R^- : R^-] \]

3. \[ [R^- : R^-] \xrightarrow{1} \text{Polymer} \]

Experimental evidence suggests segmental diffusion is the rate controlling step under most conditions. As a result, \( k_t \) for a particular polymer would be expected to be a function of radical conformation, radical size and solution viscosity. The former is conditioned by polymer solvent interactions and is not likely to vary with dilution if the solvent and monomer are of similar chemical structure. If the solvent is thermodynamically poor, however, drastic reduction occurs in \( k_t \) with dilution and consequently an increase in fractional polymerisation rates is observed. Even in thermodynamically good solvents \( k_t \) varies with the viscosity of the solution as demonstrated by North and co-workers. Therefore, if
significant changes in viscosity occur with monomer dilution, monomer orders differing from unity are expected even if the simple polymerisation scheme discussed in the introduction applies. Thus anomalous monomer orders observed by Burnett et al. in the polymerisation of MMA in various halogenated aromatic solvents can be largely explained on the solvent viscosity factor. Yohota and Itot have modified eqn. (4) to

$$R_p = k_p \left[ M \right]^{1/3} \left( k_d [I] f / k_t^0 \right)^{1/3} \quad \ldots \ (19)$$

when $k_t^0$ is the termination constant at some standard viscosity (e.g. 1 CP). They subsequently measured the polymerisation rate of MMA at different concentrations in a range of solvents and found the results consistent with the above equation. If no allowance was made for solvent viscosity and the results analysed according to eqn. (4) various monomer orders resulted both greater and less than 1.

1.5c Propagation Step

1) The Tudos Hot Radical Theory:

Based on experimental and theoretical evidence for the relative difficulty of transferring vibrational energy between molecules, Tudos has argued that some polymer radicals produced in the exothermic propagation step may well retain their excess energy of formation until they react with a further monomer molecule:

$$P_r^* + M \xrightarrow{k_p^*} P_{r+1}^*$$

\[ \ldots \]
Thermalisation of these "hot" polymer radicals occurs by collision with both monomer and solvent, S, molecules and thus normal propagation also takes place:

\[
P_r^* + M \xrightarrow{k_c^*} P_r^* + M
\]

\[
P_r^* + S \xrightarrow{k_c^*} P_r^* + S
\]

\[
P_r^* + M \xrightarrow{k_p} P_{r+1}^*
\]

Neglecting the participation of hot radicals in termination reactions because of their low concentration, it can be shown that

\[
R_p = K \left[ I \right]^{\frac{1}{2}} [M] \tag{20}
\]

where

\[
K = k_p \left( \frac{f k_d}{k_t} \right)^{\frac{1}{2}} \left[ 1 + \frac{k_p^*}{k_c^* + k_c^*/[S]/[M]} \right]
\]

At high dilutions \([S]/[M]\) and \(K \rightarrow k_c^*\). At high \([M]\), \(K \rightarrow K_0\)

where

\[
K_0 = k_c^* \left( 1 + \frac{k_p^*}{k_c^*} \right)
\]

Thus \(K\) varies between two values irrespective of the nature of the inert solvent.
In physical terms the Tudos theory postulates that two propagations reactions can occur, involving "hot" and thermalised polymer radicals. The former add monomer at a much greater rate (i.e. $k_p^* \gg k_p$) and will be less important as dilution is increased. At low [M], "hot" radical thermalisation will be complete and only one propagation step will be involved. Thus the addition of solvent will always decrease the fractional rate of polymerisation and monomer orders greater than unity will result. The initiation exponent, however, should remain as 0.5. As hot radical effects in solution he cites the observation of Bevington and Lewis\textsuperscript{11} that 30% of the benzoyloxy radicals formed photochemically from Benzoyl peroxide are immediately decarboxylated, but in the case of radicals formed by thermal decomposition no such effect occurs.

ii) The Olive Radical Complex Theory:

Henrici-Olive and Olive\textsuperscript{12a,12b,12c,12d} have pointed out that electron affinities of typical polymer radicals are of the same order as those of such molecules as tetracyanoethylene and chloranil, which are known to form charge-transfer complexes with typical solvents used in vinyl polymerisation. These authors suggest that polymer radicals can form complexes with both solvent and monomer molecules, only the latter complex leading to propagation. The concentrations of the complexes are proportional to their life times and to the concentration of monomer and solvent. Hence the ratio of the concentration of the monomer, $PM^*$ and solvent $PS^*$, complexes can be shown to be
Since only polymer monomer complexes can propagate, the rate of polymerisation is

\[ R_p = k \left[ \frac{[PM]}{[PS]} \right] = k \left[ \frac{[P]}{[S]} \right] \frac{[M]}{[S] + [M]} \]

where \([P]\) is the total concentration of complexed radicals. In bulk monomer, all polymer radicals are complexed with monomer. Hence

\[ R_{p0} = k \left[ P \right] \]

\[ = k_p \left[ P \right] [M_B] \]

Therefore, in solution,

\[ R_p = k_p \left[ \frac{[P]}{[M_B]} \right] \frac{[M]}{[S] \frac{[S]}{[M]}} \]

If \([M_B] \approx [M] + [S]\), then Eqn.(21) shows that a monomer exponent less than unity will be obtained if \( \frac{T_s}{T_m} < 1 \) and a value greater than unity if \( \frac{T_s}{T_m} > 1 \). When \( T_s = T_m \), the "normal" monomer order of 1 is obtained. Thus rate enhancement or retardation can be attributed to the presence of the solvent, in addition to the usual dilution effect. In the Tudos theory, the initiation exponent should always be 0.5. However, one important aspect viz. the role of solution viscosity factor in influencing the overall rate of polymerisation as has been shown by Burnett et.al and Bamford and
1.6 Polymerisation at High Conversion

When polymerisation are carried to high conversions, deviations from Eqn. (4) generally become more pronounced. As discussed earlier, a number of possible complications e.g. primary radical termination and radical cage effects, transfer to polymer and geminate polymer radical recombination may arise. Nevertheless, in most cases, deviations from ideal behaviour can largely be attributed to viscosity effects. Further, in addition to the normal "T^0 effect", the effect of "microviscosity" as has been pointed out by North may occur in the high conversion polymerisation of certain monomers.

1.7 Electro-initiated Polymerisation

Electro-polymerization is an electron transfer process in which the active centres in the monomer molecule is produced as a consequence of electrode reaction. Under appropriate condition it may produce free-radical, anionic or cationic mechanism in some systems. If free radicals are generated, then the mechanism of polymerisation may be that of free radical polymerisation where rate constants and the kinetics law of the same may be applied. Similar is the case if ionic species are generated at the electrodes.

An electrode may be thought to act as a sink (anodic oxidation) or a source (cathodic reduction) of electrons and the "electron
activity can be varied within wide limits by varying the potential between the electrode and the electrolyte. According to Eberson\textsuperscript{15} the electrode surface can be regarded as an aggregate of orbitals to or from which electron can be transferred; the energies of these orbitals is reflected in the electrode potential. Overlap between an electrode orbital and a suitable molecular orbital in the organic molecule will result in an electron transfer in either direction of the corresponding energy levels are properly related to each other, i.e. if the electrode potential is positive (or negative) enough to allow removal of one or possibly two electrons from the highest occupied molecular orbital of the molecule (or supply of one or two electrons to the lowest empty molecular orbital). In an ideal case, the result of electron transfer will be a radical, cationic or anionic intermediate, which after leaving the electrode surface will undergo further chemical changes in the solution surrounding the electrode, or in favourable cases accumulate in the solution. A wide choice of solvents and added reagents would thus, in principle, provide us with a variety of synthetic possibilities once a particular intermediate has been generated by an electrode process. This new method of production of initiating species would thus lead to a reaction which is no longer dependent on temperature or the initial concentration of reactants. Thus the generation of free radicals may be controlled, the molecular weight of the polymer may be programmed by the control of electrolytic current and also control of reactions may be achieved through external sources.
The fundamental role of electrolyte is not yet established but by changing the electrode material it has been observed that the rate of reaction is hampered. Electrodes may be considered as acid or base of variable strength. The electrodes can also play a significant role in the synthesis through the adsorption of products. The initiating species may also be generated by the passage of current to the monomer whereby direct addition of electron to monomer result the initiating species or by the reaction of the electrolytic salt present in the monomer.

The discovery of electrochemical initiation arrived from the conception of Michael Faraday's electrolyte reaction in 1834. The name of Kolbe is perhaps more properly associated with the conceptual ideas which govern the process. By 1845 he had carried through chemical synthesis by electrical means and shortly thereafter, the electrolysis monoolefinic aliphatic acid to hydrocarbons. The development of electrochemical reactions is much more prominent in last few years. The process can broadly be divided into two types (1) Cathodic (2) Anodic.

For the cathodic reaction, generation of free-radical and radical-anion, and formation of unstable monomer active catalyst are visualised from the corresponding references.

A. Generation of free radical.

1. \( H^+ + e \rightarrow H^- \) \[ \text{... (i)} \]
2. \( \text{CH}_3 - \text{C} - \text{C}_6\text{H}_5 + e \rightarrow \text{CH}_3 - \text{C} - \text{C}_6\text{H}_5 \text{(-pinacol)} \) ... (ii)

3. \( \text{R}_0 \text{O}_0 \text{R} + e \rightarrow \text{R}^\bullet + \text{O}_2 \text{R}^- \) ... (iii)

4. \( \text{H}_2\text{O}_2 + e \rightarrow \text{OH}^- + \text{OH}^\bullet \) ... (iv)

B. Generation of radical-anion.

1. Indirect electron transfer to monomer.
   \( \text{Na}^+ + e \rightarrow \text{Na} \)
   \( \text{Na} + \text{M} \rightarrow \text{Na}^+ + \text{M}^- \) ... (v)

2. Direct electron transfer to monomer.
   \( \text{M} + e \rightarrow \text{M}^\bullet^- \) ... (vi)

C. Formation of unstable monomer.

\( \begin{array}{c}
\text{N} \\
\text{N} + e \\
\text{N} = \text{N} \text{ or } \text{N} \cdot
\end{array} \) ... (vii)

D. Formation of active catalyst (or redox).

1. \( \text{Fe}^{+3} + e \rightarrow \text{Fe}^{+2} \) ... (viii)
   \( \text{Fe}^{+2} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{+3} + \text{OH}^- + \text{OH} \)

2. \( \text{Ni}^{+2} + e \rightarrow \text{Ni}^0 \) (Butadiene Oligomerization) ... (ix)

The free-radicals are generated by discharge of proton, peroxides and easily reducible compounds at the cathode according to...
equations. The radical-anion of monomer is obtained by both direct and indirect electron reaction, followed by interaction with the monomer.

For the anodic reaction, generation of free-radical and radical-cation, and oxidative condensation are revealed.

E. Generation of free-radical (by Kolbe's reaction).

\[ \text{CH}_3\text{COO}^- + (-e) \rightarrow \text{CH}_3\text{COO}^* \rightarrow \text{CH}_3^* + \text{CO}_2 \]  \hspace{1cm} \ldots \text{(x)}

F. Generation of radical cation.

1. \[ \text{ClO}_4^- + (-e) \rightarrow \text{ClO}_4^* \]  \hspace{1cm} \ldots \text{(xi)}

\[ \text{ClO}_4^* + \text{M} \rightarrow \text{ClO}_4^- + \text{M}^+ \]

2. Discharge of monomer

\[ \text{M} + (-e) \rightarrow \text{M}^+ \]  \hspace{1cm} \ldots \text{(xii)}

G. Oxidative condensation polymerisation.

\[ \text{F}^- + (-e) \rightarrow \text{F}^* \]

\[ \text{F}^* + \text{C}_6\text{H}_6 \rightarrow \text{FH} + \text{C}_6\text{H}_5^* \]

\[ 2\text{C}_6\text{H}_5^* \rightarrow \text{C}_6\text{H}_5 - \text{C}_6\text{H}_5 \]  \hspace{1cm} \ldots \text{(xiii)}

H. Ring opening polymerisation by the reaction according to eqn.(xi).

Generation of free-radicals by Kolbe's reaction is well-known (eqn.x). Formation of a free radical-cation of monomer (eqn.xi) has never been proved and is only a possible conjecture from the right
reverse consideration of radical-anion formation at the cathode (eqn.vi), although the perchlorate anion has actually been found to yield an unstable perchlorate free-radical by discharge at the anode. Nor it is certain that monomer radical-cation is formed by the direct discharge from the anode (eqn.xii). The ring opening polymerization of oxides, caprolactum and isocyanides is also initiated on the electrode.

A brief account of the characteristics, potentialities and advantage of the electrochemical polymerization from the point of view of polymer chemistry is summarized below:

(i) Lower cost of electricity compared to chemical activation agents.
(ii) The electrolytic reaction generally participates in the initiation process and not in the propagation step.
(iii) By the regulation of external current, the source of energy, the initiation step can be controlled and consequently the final properties are controlled.
(iv) In the living polymer system, the termination of growing ends as well as initiation can be controlled by the passage of electric current.
(v) The electrolytic reduction and oxidation of appropriate ends lead to condensation polymerization.
(vi) An active species may be generated "in situ" by means of
electrode reaction thereby handling of reactive chemicals (azo-compounds, benzoyl peroxide, organometalics BF₃, alkali metals) can be avoided.

(vii) Simpler purification of electrolytes and electrodes compared to that of reactive chemicals.

(viii) The wide range of reactivity of an electrode in a given electrolyte solution and at a fixed temperature which is directly related to and controlled by the electrode.