CHAPTER-1

GENERAL INTRODUCTION

1.0 Introduction

Vinyl monomers are known to undergo polymerization through a chain reaction process which may be activated thermally or photochemically or by a host of catalysts or initiators.

The overall polymerization reaction is a typical chain process which is set off by active centres of free radical or ionic types. Free radical chain mechanism for the polymerization of vinyl and related monomers is primarily due to Taylor[1] and Staudinger[2]. Chain mechanism for the polymerizations involving ionic intermediates was proposed by Whitmore[3] and Price[4]. According to Staudinger[5], activation of a monomer molecule (CH_2=CHX) leads to the opening up of the double bond and then the activated molecule reacts with successive monomer molecules to give intermediates with free valences at the both ends of the molecule viz. $\overset{\bullet}{C}H_2$-CHX-$(CH_2$-CHX$)_n$-CH_2-$\overset{\bullet}{C}HX$. Though Staudinger simply suggested that no end-group was necessary to saturate the terminal valences of polymer chains, it is now well established that all polymers bear specific, well characterizable end groups.

1.1 Theory of Free-Radical Vinyl Polymerization :

Flory[6] showed that the radical polymerization proceeds by the steps of initiation, propagation and termination. Initiator molecules in a free radical vinyl polymerization
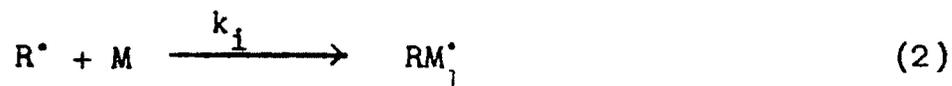
decompose into active radical species which in turn attack
the π-bonds of the unsaturated monomer molecules forming
new radicals. A new radical centre called the chain radical
adds to another monomer molecule and the process is repeated
such that many more monomer molecules successively add to
the growing chain at a fast rate. Polymer growth is termi-
nated at some point by the destruction of the reactive
(radical) centre by an appropriate reaction depending on
the type of reactive centre and the particular reaction
conditions.

The polymerization of a vinyl monomer M, induced by
a free radical initiator I, may be schematically represented
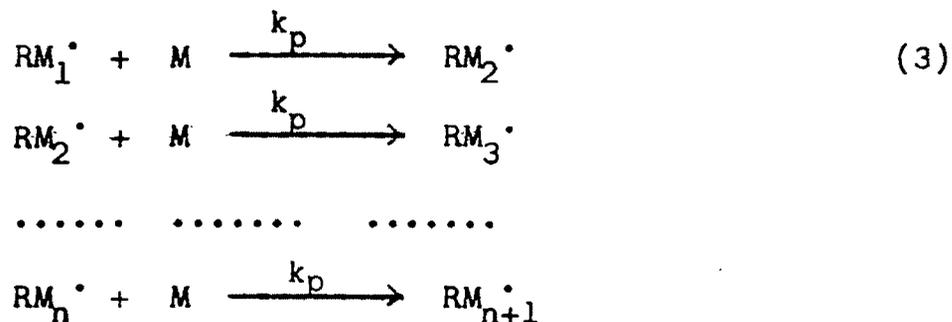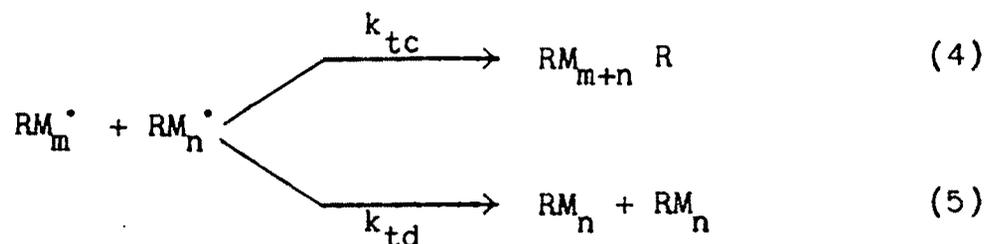as follows :

i) Initiator decomposition :

$$I \xrightarrow{\ k_d\ } 2R^{\cdot} \tag{1}$$

followed by chain initiation :

$$R^{\cdot} + M \xrightarrow{\ k_i\ } RM_1^{\cdot} \tag{2}$$

ii) Chain propagation :

$$RM_1^{\cdot} + M \xrightarrow{\ k_p\ } RM_2^{\cdot} \tag{3}$$

$$RM_2^{\cdot} + M \xrightarrow{\ k_p\ } RM_3^{\cdot}$$

$$\cdots\cdots \quad \cdots\cdots \quad \cdots\cdots$$

$$RM_n^{\cdot} + M \xrightarrow{\ k_p\ } RM_{n+1}^{\cdot}$$

iii) Chain termination :

$$RM_m^\bullet + RM_n^\bullet \begin{cases} \xrightarrow{k_{tc}} RM_{m+n} \; R & (4) \\ \xrightarrow{k_{td}} RM_n + RM_n & (5) \end{cases}$$

where $R^\bullet$ is a free-radical generated from the initiator I, and $RM_1^\bullet$, $RM_2^\bullet$, $RM_3^\bullet$ etc are the growing polymer chains, each bearing a radical centre at the growing chain-end and RM_m, RM_n and $RM_{m+n}R$ are the dead polymer molecules obtained.

It is clear from the above scheme that the initiator fragments (R) form the "end-groups" by sealing one or both ends of the polymer chains. According to the scheme represented above, the initiator I first decomposes into a pair of primary radicals $R^\bullet$ as in equation (1) and then each primary radical $R^\bullet$ attacks a monomer molecule M to yield a chain-radical $RM_1^\bullet$ as in equation (2). These two steps are characterized by rate constants k_d, the rate constant for decomposition of the initiator and k_i, the rate constant for chain initiation respectively. The growth of the polymer molecule by the addition of monomer to $RM_1^\bullet$ and the successive radicals, as represented in equation (3) is characterized by rate constant k_p, the rate constant for propagation reaction, where the radical reactivity is assumed to be independent of chain length and extent of reaction. The propagation reaction may then be simply written as $M^\bullet + M \xrightarrow{k_p} M^\bullet$.

The cessation of growth of the radicals occurs through bimolecular reactions involving in each case a pair of chain-radicals and this may take place by two different mechanisms viz. termination by combination, equation (4) and termination by disproportionation, equation (5) respectively. For most kinetic purposes the bimolecular nature of the termination process is important, irrespective of whether coupling or disproportionation is prevalent. The overall mechanism of termination reaction may be expressed as,
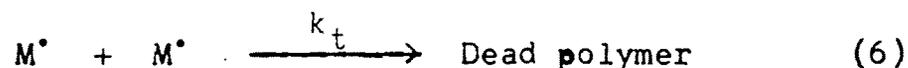
$$M^\bullet \; + \; M^\bullet \quad \xrightarrow{\quad k_t \quad} \quad \text{Dead polymer} \qquad (6)$$

and the overall rate constant of termination, k_t may be expressed as,

$$k_t \; = \; k_{tc} \; + \; k_{td} \qquad (7)$$

It is evident from the above scheme that dead polymers formed by combination would contain two initiator fragments (R) per polymer molecule as chain-ends, whereas disproportionation would lead to polymers having only one initiator fragment (R) per molecule and fifty percent of polymer molecules would contain one unsaturation at one of their chain-ends.

According to equations (1) and (2), the rate of initiation (R_i) of chain radicals may be expressed as :

$$R_i \; = \; (d \, [M^\bullet]/dt)_i \; = \; 2 \, f k_d [I] \qquad (8)$$

where $[M^\bullet]$ represents the total concentration of all chain radicals irrespective of their size, $[I]$ is the concentration

of the initiator and 'f' is the initiator efficiency.

The rate of chain termination (R_t) from equation (4) or (5) may be written as :

$$R_t = -(d[M^\bullet]/dt)_t = 2 k_t[M^\bullet]^2 \qquad (9)$$

The factor '2' enters as a result of disappearance of two radicals at each incidence of the termination reaction.

Assuming a steady-state condition for the chain process and bimolecular termination of growing polymer chains, the rate of propagation, R_p which in effect may be taken as the overall rate of polymerization, is given by the following expression[6] :

$$R_p = k_p \left(\frac{f k_d}{k_t}\right)^{1/2} [I]^{1/2} [M] \qquad (10)$$

1.2 Kinetic chain length and degree of polymerization

The kinetic chain length $\hat{\gamma}$, represents the average number of monomer molecules consumed by a particular active centre from its initiation to its termination step. Assuming bimolecular termination, $\hat{\gamma}$ may be expressed as follows[6] :

$$\hat{\gamma} = \frac{k_p^2}{2 k_t} \cdot \frac{[M]^2}{R_p} \qquad (11)$$

The kinetic chain-length is thus inversely proportional to the radical concentration or the rate of polymerization when termination is bimolecular. So an increase in the rate of

polymerization causes lowering of kinetic chain length, which is directly related to the average number of monomer molecules contained in a polymer molecule, i.e., the degree of polymerization ($\bar{P}_n$).

The mean molecular chain-length or degree of polymerization, $\bar{P}_n$, is the average number of monomer molecules consumed for each dead polymer formed, hence for termination by mutual combination

$$\bar{P}_n = 2\gamma \qquad (12a)$$

and for termination by disproportionation

$$\bar{P}_n = \gamma \qquad (12b)$$

When termination by disproportionation and combination both take place simultaneously, it can be shown as[7,8]

$$\bar{P}_n = \frac{2(Y+1)}{(Y+2)} \cdot \gamma \qquad (12c)$$

where Y is the ratio of combination to disproportionation.

1.3 k_p^2/k_t ratio :

k_p^2/k_t is an important parameter in the chain polymerization kinetics because the polymerization rate may be predicted for any value of initiation rate from the value of the ratio. It also gives the relative order of polymerizability of different monomers at a given rate of chain initiation and its value can be obtained from the following expression, obtained by combining (11) and (12c),

$$\frac{1}{\bar{P}_n} = \left(\frac{Y+2}{Y+1}\right) \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} \qquad (13)$$

In the most simplified case, i.e., in absence of any side reactions, a plot of $1/\bar{P}_n$ vs. $R_p/[M]^2$ would reasonably give a straight line, from the slope of which the value of k_p^2/k_t can be obtained .

1.4 Chain transfer

In addition to the usual reaction steps i.e., initiation, propagation and termination, occurrence of certain other side reactions limiting the growth of polymer molecules without really affecting the rate of polymerization is often indicated[9]. These reactions are termed as chain transfer reactions. Chain transfer usually lowers the $\bar{P}_n$ value. A chain transfer reaction proceeds via transfer of the free radical centre from a growing chain to a molecule present in the system to generate a new radical which propagates the chain process in the normal manner.

The effect of different chain-transfer reactions on the degree of polymerization, $\bar{P}_n$, can be suitably represented by the following expression[10],

$$\frac{1}{\bar{P}_n} = (\frac{Y+2}{Y+1}) \frac{k_t}{k_p^2} \cdot \frac{R_p}{[M]^2} + C_I \frac{[I]}{[M]} + C_M + C_S \frac{[S]}{[M]} + C_X \frac{[X]}{[M]} \quad (14)$$

where C_I, C_M, C_S and C_X are chain transfer constants due to initiator, monomer, solvent or any other species, X present in the system respectively.

In the presence of normal chain transfer reactions as above, the degree of polymerization is affected, while the rate of polymerization remains unaffected[11,12]. It is in the

presence of a degradative chain transfer process that both degree of polymerization and rate of polymerization are lowered[13,14].

1.5 Inhibition and retardation

Inhibition is a process by which the polymerization reaction is completely stopped or inhibited and retardation is a process by which the rate of polymerization is reduced or retarded. Substances used for inhibition and retardation are known as inhibitors and retarders respectively. Benzoquinone[15] and oxygen[16] are effective inhibitors for most free-radical polymerizations while nitrobenzene and nitrosobenzene[17,18] are examples of retarders.

1.6 Photopolymerization

Photochemical reactions can also lead to initiation of free radical polymerizations[19,20]. Photoinitiation may be considered under three broad categories. a) Uncatalyzed, b) Catalyzed and c) Sensitized photoinitiation.

(a) Uncatalyzed photopolymerization :

On photoactivation the monomer M may generate excited species M* by absorbing light quanta of specific wave length and may subsequently decompose into radicals by homolysis or related mechanisms which may then contribute to chain initiation

$$M \xrightarrow{h\nu} M^* \longrightarrow R^{\bullet} + R^{\bullet'} \qquad (15)$$
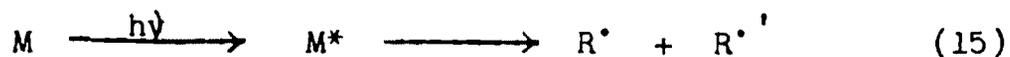
Just as in purely thermal initiation so also in uncatalyzed photoinitiation the exact identity of the primary radicals as in the above reaction (15) are not yet established with any degree of certainty.

The rate of photochemical initiation may be expressed as :

$$R_i = 2 \phi I_a \qquad (16)$$

simply by replacing $k_d[I]$ of eq.(8) with the intensity of active radiation, I_a and replacing f with ϕ for the photochemical polymerization where ϕ is interpreted as the quantum yield for chain initiation or radical generation which actually stands for the number of pairs of chain radicals generated per quantum of light absorbed.

Assuming for simplicity that the incident light intensity does not measurably vary with thickness of the reaction mass, I_a may be expressed as

$$I_a = \epsilon I_o [M] \qquad (17)$$

The rate of polymerization for uncatalyzed photopolymerization may then be expressed as

$$R_p = (k_p/k_t^{1/2})(\phi\epsilon I_o)[M]^{3/2} \qquad (18)$$

here, ϵ is the molar absorption co-efficient of the active radiation.

(b) Catalyzed photopolymerization

For photopolymerization using a photoactive additive

as a catalyst or initiator in the monomer, the initiator readily undergoes photolysis to generate radicals which then initiate the chain polymerization.

Many thermal initiators which produce specific radicals from thermal homolytic cleavage of specific bonds also under-go photolytic decompositions to produce the same radicals. Photoactivation allows the use of a wider range of chemicals as photopolymerization initiators in comparison with the thermally catalyzed process. This is consequent to the higher selectivity of the photolytic homolysis. For many compounds other than the more common initiators known, thermal homo-lysis occurs at too high a temperature and it often leads to the generation of a wide spectrum of radicals as various chemical bonds break up randomly.

The rate of initiation using a photoinitiator, I is given by,

$$R_i = 2 \, \phi \, \epsilon \, I_o \, [I] \tag{19}$$

and the rate, R_p of the related photopolymerization is given by

$$R_p = k_p/k_t^{1/2} \, (\phi \, \epsilon \, I_o)^{1/2} \, [I]^{1/2} \, [M] \tag{20}$$

(c) Photopolymerization using a photosensitizer

Photosensitizers are generally employed in order to bring about effective homolysis of monomers or initiators which otherwise donot undergo sufficient photoexcitation at the frequency of light made available to the system. The

photosensitizer (Z), because of its being highly photosensitive readily gets excited on exposure to light to Z* which then carries the energy absorbed to the initiator or monomer molecules and transfers the energy to them to form excited initiator or monomer species.

$$Z* + I \text{ (or M)} \longrightarrow Z + I* \text{ (or M*)} \qquad (21)$$

The excited species thus formed undergo homolysis to form chain initiating radicals. Aromatic ketones such as benzophenone are one kind of most widely used photosensitizers in organic photochemistry and they have been very widely used by many workers as sensitizers in many uncatalyzed or catalyzed photovinyl polymerization.

1.7 Energetic characteristics (Activation energy) :

Increase of temperature usually increases the polymerization rate and decreases the polymer molecular weight. The quantitative effect of temperature is complex, since R_p and $\bar{P}_n$ depend on a combination of three rate constants, namely k_d, k_p and k_t. The apparent activation energy E_a for overall polymerization is given by,

$$E_a = E_d/2 + (E_p - E_t/2) \qquad (22)$$

where the subscripts d, p and t have their usual significance. The activation energy for the spontaneous decomposition of most of the commonly used free-radical initiators is in the

range of 30-35 k cal/mole[21]. The E_p and E_t values for most

of the monomers are in the range of 5-10 k cal/mole and

2-5 k cal/mole respectively[21]. The overall activation energy

for most of the polymerizations initiated by thermal decompo-

sition of initiator is therefore close to 20 k cal/mole. For

redox polymerizations the activation energy is much lower[22]

(10 k cal/mole).

For purely photochemical initiation, the initiation

step is temperature dependent, and E_d = 0, since the energy

for initiator decomposition is supplied by light quanta. The

apparent activation energy for overall photomerization is

about 5 k cal/mole. This low value of E_a indicates that R_p

of photopolymerization will be less sensitive to change in

temperature compared to thermal polymerization. Again, most

of photoinitiators may also decompose thermally, particularly

at higher temperatures, the initiators may thus also undergo

appreciable thermal decomposition in addition to photochemical

decomposition. In such a case, both thermal and photochemical

initiations must be taken into consideration.

1.8 Non-ideality in the kinetics of radical vinyl polymeri-
zation

The general behaviour of free radical chain polymeriza-

tion of vinyl monomers is that the rate of free radical vinyl

polymerization should be proportional to the first power of

monomer concentration and to the square-root of initiator

concentration though reports on deviations from this general relationship are also abundant[23-41]. A number of side-effects, not considered in the normal polymerization scheme, have been put forward in order to explain the observed kinetic deviations and they are :

(a) complex formation between monomer and initiator[23-29].

(b) cage effect[30,31].

(c) Primary radical termination[32-35].

(d) Solvent participation in polymerization leading to enhancement or retardation in rate[35-40].

(e) Degradative chain transfer involving initiator molecules or other additives[13,14,41].