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Polymer Chemistry

DSE-4T

Narajole Raj College

Department of Chemistry

Kinetics of Polymerization

Lecture Note-3

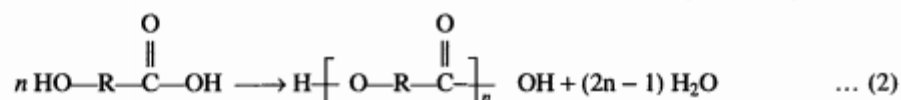
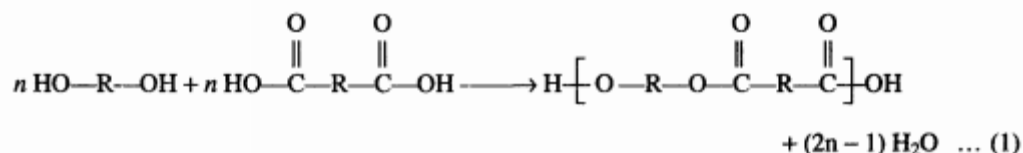


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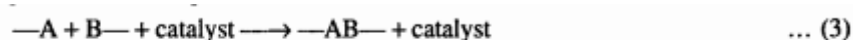
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A. KINETICS OF LINEAR CONDENSATION POLYMERISATION

It is assumed that most step polymerisations involve bimolecular reactions as key mechanistic process. Typical examples of the product of polyesters are given in equations (1) and (2).



We know that the reaction between two functional groups (in the above case the groups are $-\text{OH} \equiv \text{B}$ and $-\text{COOH} \equiv \text{A}$) is independent of the chain length of the molecules attached to the two functional groups except in the initial stages of the reaction. Thus, the reaction given in equations (1) and (2) may be represented by the general chemical equation (3) and the general kinetic equation (4).



$$\text{Rate} = k [\text{A}] [\text{B}] [\text{catalyst}] \quad \dots (4)$$

If the esterification reaction is acid catalysed (*i.e.*, H^+) [catalyst] is usually taken to be (*i.e.*, H^+) and two mechanisms should be considered since H^+ ions can be supplied either from an external source (external catalysis) or provided internally by the dissociation of the carboxylic acid (self catalysis).

If stoichiometry of the functional groups A and B is assumed (*i.e.*, $[\text{A}] = [\text{B}]$ and $\text{A} = \text{B}$), the kinetic equation (4) may be rewritten as equation (5).

$$\text{Rate} = -\frac{d(\text{A})}{dt} = k [\text{H}^+] [\text{A}]^2 \quad \dots (5)$$

It is also possible, by monitoring the loss of the acid groups, A. *e.g.*, by titration with base, to estimate the concentration (or number of molecules) of carboxylic acid present initially and at some time t and hence to determine the degree of polymerisation \overline{X}_n and make an estimate of the number average molar mass \overline{M}_n .



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$$\bar{X}_n = \frac{N_0}{N_t} \quad \dots (6)$$

$$\bar{M}_n = \bar{M}_0 \bar{X}_n \quad \dots (7)$$

In equation (6), N_0 represents the number of carboxylic groups present initially and N_t represents the number of carboxylic group at time t . In equation (7) \bar{M}_0 is the value of the mean molar mass and is given by equation (8).

$$\bar{M}_0 = \frac{\text{Molar mass of the repeat unit}}{\text{Number of monomer units in the repeat unit}} \quad \dots (8)$$

Also, assuming equal number of the functional groups A and B (*i.e.*, stoichiometry) allows a deduction as to how far the step reaction has proceeded towards producing polymer (*i.e.*, extent of reaction, P) in a given period of time (equation 9).

$$P = \frac{\text{Number of carboxylic acid groups which have reacted}}{\text{Number of carboxylic acid groups initially present}} \quad \dots (9)$$

In terms of the number of carboxylic groups, equation (9) can be rewritten as equation (10)

$$P = \frac{N_0 - N_t}{N_0} \quad \dots (10)$$

In terms of the concentration of the functional groups, equation (10) can be rewritten as equation (10a).

$$P = \frac{C_0 - C}{C_0} \quad \dots (10a)$$

In equation (10a) C_0 represents the concentration of the carboxylic groups at $t = 0$ and C is the concentration at time t .

Or Combining equations (6) and (10) gives equation (11).

$$\bar{X}_n = \frac{N_0}{N_t} \quad \dots (6)$$

$$P = \frac{N_0 - N_t}{N_0} \quad \dots (10)$$

$$\bar{X}_n = \frac{1}{(1 - P)} \quad \dots (11)$$

Similarly equation (10a) can be rewritten as follows:



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$$P = \frac{C_0 - C}{C_0}$$

$$P = 1 - \frac{C}{C_0}$$

$$\frac{C}{C_0} = 1 - P$$

$$C = C_0(1 - P) \quad \dots (12)$$

$$N_t = N_0(1 - P) \quad \dots (13)$$

SELF CATALYSIS POLYESTERIFICATION

In self catalysis polymerisation polyesterification reactions, the concentration of $[H^+]$
 $= [A] = [C]$

Thus equation (5) can be rewritten as equation (14)

$$\frac{-d[A]}{dt} = k[A]^3 \quad \dots (14)$$

$$\frac{-dc}{dt} = k[C]^3 \quad \dots (14a)$$

On integration, equation (14a) gives

$$2kt = \frac{1}{C^2} - \frac{1}{C_0^2} \quad \dots (15)$$

In this equation, C_0 is the 'concentration of the functional group at time $t = 0$ and C is the concentration at time t .

Combining equations (12) and (15) gives equation (16).

$$2kt = \frac{1}{[C_0(1 - P)]^2} - \frac{1}{C_0^2}$$
$$2kt C_0^2 = \frac{1}{(1 - P)^2} - 1 \quad \dots (16)$$

Equation (16) implies that a graphical plot of $\frac{1}{(1 - P)^2}$ versus time must be linear. Experimentally this has been found to be the case. **Fig. 1** represents a plot for the reaction between adipic acid and diethylene glycol and diethylene glycol (DE) and caproic acid (C).



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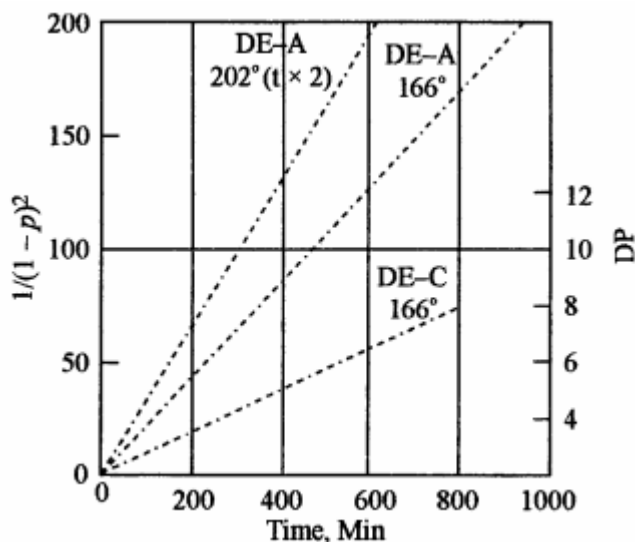


Fig. 1. Reaction of diethylene glycol with adipic acid (DE-A) and of diethylene glycol with caproic acid (DE-C). Time values at 202°C have been multiplied by two

For a simple esterification reaction, which proceeds without any side reaction, the degree of polymerisation \bar{X}_n may be related to P by equation (11). Combining equations (11) and (12) gives equation (17).

$$\bar{X}_n = \frac{1}{1-P} \quad \dots (11)$$

$$1-P = \frac{C}{C_0} \quad \dots (12)$$

$$\bar{X}_n = \frac{1}{1-P} = \frac{C_0}{C} \quad \dots (17)$$

Combining equations (16) and (17) gives equation (18).

$$2kt C_0^2 = \frac{1}{(1-P)^2} - 1 \quad \dots (16)$$

or $2kt C_0^2 + 1 = \frac{1}{(1-P)^2}$

or $2kt C_0^2 + 1 = \bar{X}_n^2$
 $\bar{X}_n^2 = 2kC_0^2 t + 1 \quad \dots (18)$

In equation (18), the \bar{X}_n appears as the second power and the time as the first power and hence the 'polymer molecular weight will increase only slowly (see equation (7))

$$\left(\frac{M_n}{M_0}\right)^2 = 2kC_0^2 t + 1 \quad \dots (19)$$



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B. FREE RADICAL POLYMERISATION

As already stated, chain-growth polymerisation takes place by a chain reaction, which consists of three main steps : initiation, propagation and termination.

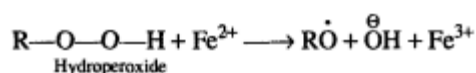
There is formation of active species in initiation step. This active species is a free radical which is formed by the homolytic bond fission of the π - bond of the monomer. This process requires energy. This process can be brought about by the action of heat, light or by adding to the system extraneous free radicals or substances (initiators) that break down readily into free radicals. Depending on the method of formation of free radicals (active species) the polymerisation is said to be thermally, photochemically or chemically initiated.

Thermally initiated polymerisation is a polymerisation wherein the monomer molecule is activated by heat. This is a very important method because in practice polymerisation very often involves heating. However, in the pure form thermal polymerisation is not very probable; it is usually accompanied by polymerisation under the action of catalyst or initiators.

Photochemical polymerisation is a polymerisation in which the monomer molecule is activated as a result of the absorption of UV light. Photochemical polymerisation may occur at temperature where at polymerisation initiated by other methods does not proceed.

Chemically initiated polymerisation, one of the most popular methods, consists in activating the monomer molecules by substances capable of decomposing into free radicals when heated. Such substances include inorganic and organic peroxides, hydroperoxides, and diazo compounds.

Oxidation-reduction initiation is often used in polymerisation. Here free radicals formed as a result of an oxidation-reduction reaction initiates the polymerisation, *e.g.*,



Oxidation-reduction reaction require much less activation energy than the thermal of peroxides to free radicals (approx. 10 kcal/mol as compared to 30-35 kcal/mole). This makes it possible to carry out the polymerisation at lower temperatures.

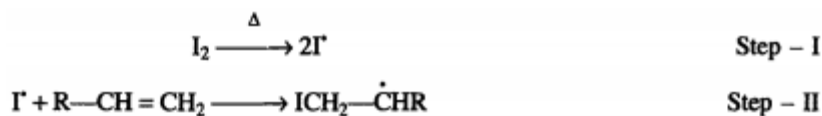
The most important free radical polymerisation is the chemically initiated polymerisation. Activation (termed 'initiation' for polymers) is produced by splitting an



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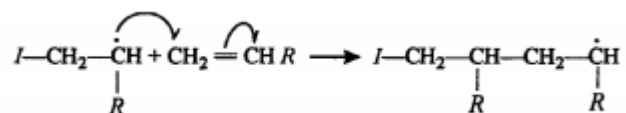
initiator molecule I_2 homolytically, usually by thermal degradation and allowing the odd electron species to react with the monomer ($CH_2=CH-R$), by opening the double bond. The initiation of polymerisation is therefore a two-step sequence.



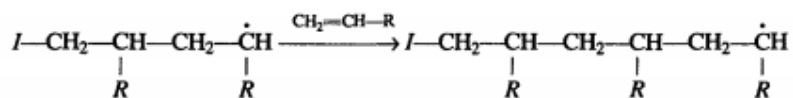
Here the step-I is endothermic process but step-II is exothermic process.

Propagation

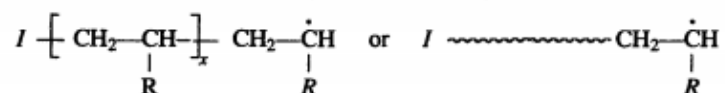
In the propagation step, the radical site at the first monomer unit attacks the double bond of a fresh monomer molecule.



This result in the linking up of the second monomer unit to the first and the transfer of the radical site from the first monomer unit to the second. It should be noted that this chain still contains a radical site and therefore, attack yet another monomer with a simultaneous transfer of the radical site to the new monomer.



This process involving a continuing attack on fresh monomer molecules which, in turn, keep successively adding to the growing chain one after another is termed propagation. Thus in propagation step the radical of the initiation step adds further monomer molecules in rapid succession to form a polymer chain. In this propagation the active centre remains, being continuously located at the end of the chain. The structure of the growing chain can be represented as follows :

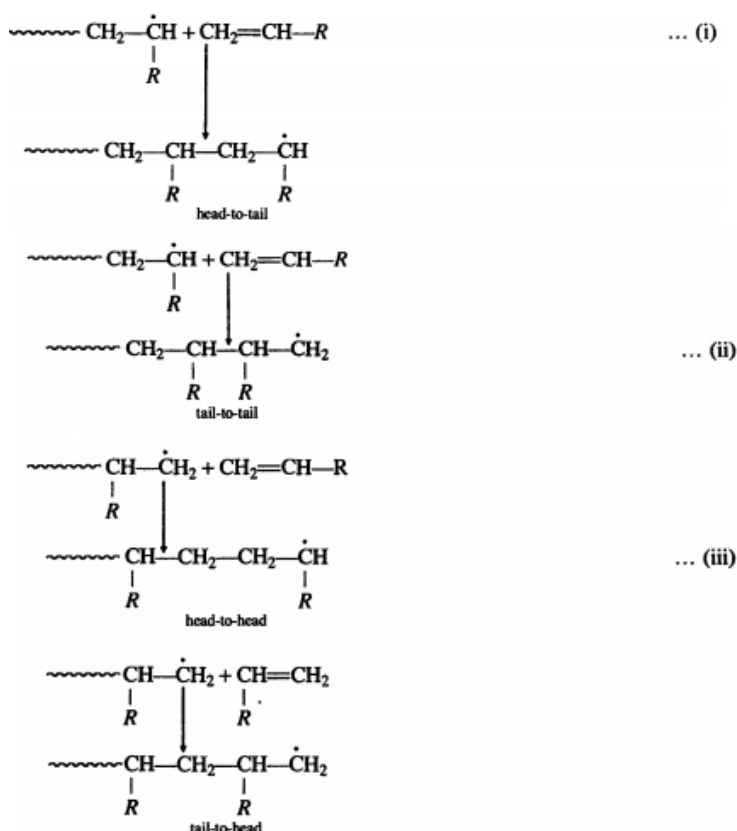


The mode of addition of the incoming monomer to the growing chain can be of the head-to tail, tail-to-tail, head to head or tail to head type. The four modes of addition can be represented as follows:



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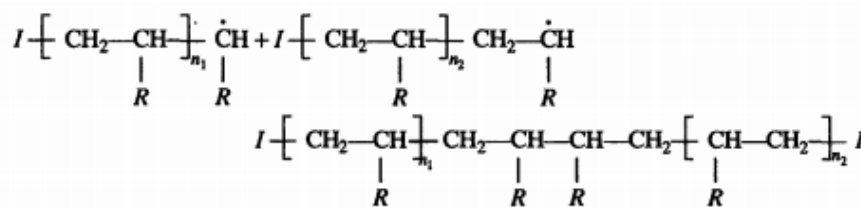


The most common mode is the head-to-tail combination.

Termination

Deactivation of the growth process is called termination. Such termination occurs commonly by reaction with another long chain radical in one of the two ways :

(i) **Combination:** In this process two radical species combine to give a **dead** polymer as follows:

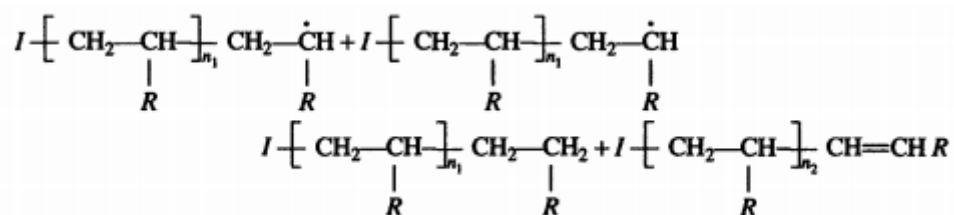


(ii) **Disproportionation** : In this process two radical species undergoes disproportionation reaction to give dead polymers as follows :

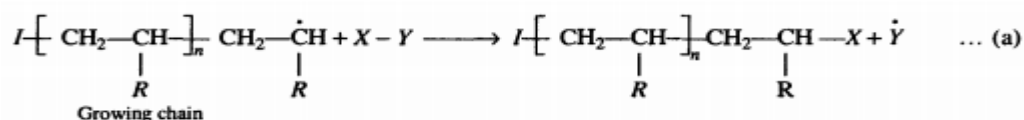


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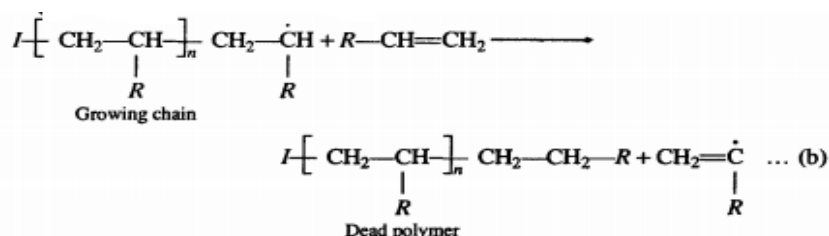
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During a polymerisation reaction both of these termination mechanisms may operate together or one only may occur to the exclusion of the other. The actual mode of termination depends on the experimental conditions and the monomer involved. Termination of a growing polymer chain may be also occur by a chain transfer reaction. In this case deactivation of the chain radical results in the formation of a new radical. Transfer reaction takes place as follows :



where XY may be monomer, polymer, solvent or added modifier. Depending on its reactivity, the new free radical (Y) may or may not initiate the growth of another polymer chain. The transfer reaction between monomer and growing polymer chain takes place as follows :



The growing chain is now terminated, but. a new free radical ($\dot{\text{Y}}$ in equation (a) and $\text{CH}_2=\text{C}-\text{R}$ in equation (b)) is formed. $\dot{\text{Y}}$ or $\text{CH}_2=\text{C}-\text{R}$ will now initiate the polymer chain growth afresh which will be followed by the chain propagation. Hence the termination of one chain growth and the initiation of a new one takes place simultaneously. It is as if the chain growth is transferred from one site to another and hence this phenomenon is called chain transfer.

Kinetics of Free Radical Addition Polymerisation

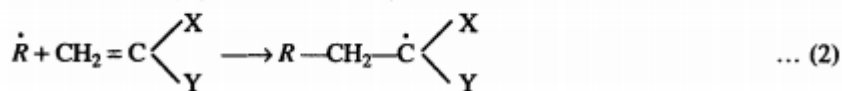
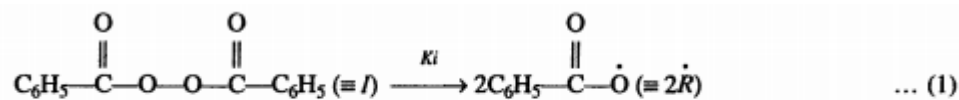
As already stated, addition polymerisation takes place by a chain-reaction, which consist of three main steps : initiation, propagation and termination.



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Initiation : Initiation takes place as follows :



The slow step in the initiation is given by equation (1).

The reaction (2) may be abbreviated and generalised to (2a)



where M stand for monomer and M_1^\bullet denotes a monomer added radical. There is only onemonomer in this radical. The rate constant for the reaction (2a) is K_i .

The slow step in the initiation is given by equation (1).

Since the product of the active centres (R^\bullet) occurs twice as fast as the loss of the initiator molecule $\left(\frac{-dI}{dt}\right)$ and not all the radicals will be involved in activating the monomers since some radicals may undergo recombination, the production of active centres is given by the equation (3).

$$R_i = \frac{d[R^\bullet]}{dt} = 2K_i f [I] \quad \dots (3)$$

where f represents initiator efficiency ($0 < f < 1$). The value of f which is usually between 0.6 and 1.0 gives the efficiency of initiator. The value of 0.6 indicates that only 60% of the radical generated have effectively initiated the chain growth, the remaining 40% being lost as side products.

Propagation: By definition, a propagation step in a chain reaction is one in which products are formed, and the site of the reactive center changes but the number of active centers is not changed. The propagation steps can be represented as follows :





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Each reaction in the sequence involves the addition of a monomer to a monomer-ended radical, and each is assigned the same rate constant K_p on the reasonable assumption that the rate of addition reaction does not depend on the size of the participating macroradical.

Reaction (4c) is a bimolecular reaction and K_p is therefore, a second order rate constant with units of $(\text{conc})^{-1} (\text{time})^{-1}$. The rate of propagation is given as follows :

$$R_p = K_p [\dot{M}] [M] \quad \dots (5)$$

where \dot{M} stands for the sum of the concentration of all monomer-ended radicals (*i.e.*, concentration of the growing chain) in the system and $[M]$ represents the concentration of monomer.

Termination : Termination or deactivation produce dead polymer. While in general there are two forms of termination, namely addition and disproportionation, the coupling of two radicals together is far most common. Here termination will be restricted to the combination (addition) reaction shown below as follows :



The corresponding rate equation for the termination process is given by equation (7)

$$-\frac{d[\dot{M}]}{dt} = R_t = 2K_t [\dot{M}]^2 \quad \dots (7)$$

Factor 2 in equation (7) comes from the fact that two chains are terminated in such a combination step.

RATE OF POLYMERISATION

The assumption that the rate of initiation equals the rate of termination is called the steady state assumption. It is equivalent to two following equations :

$$R_i = R_t \text{ at steady state} \quad \dots (8a)$$

$$\frac{d[\dot{M}]}{dt} = 0 \text{ at steady state} \quad \dots (8b)$$

Since the steady rate is reached soon after polymerisation starts we can assume without significant error that it applies to the whole course of the polymerisation. Substituting equations (3) and (7) into equation (8a).



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$$2f K_i [I] = 2K_t [\dot{M}]^2$$

Hence
$$[\dot{M}] = \left(\frac{f K_i}{K_t} [I] \right)^{1/2} \quad \dots (9)$$

From equation (5) we get the value of $[\dot{M}]$ as

$$R_p = K_p [\dot{M}] [M] \quad \dots (5)$$

$$[\dot{M}] = \frac{R_p}{K_p [M]} \quad \dots (10)$$

On substituting this value $[\dot{M}]$ in equation (9), we get

$$[\dot{M}] = \left(\frac{K_i f [I]}{K_t} \right)^{1/2} \quad \dots (9)$$

$$\frac{R_p}{K_p [M]} = \left(\frac{K_i f [I]}{K_t} \right)^{1/2} \quad \dots (10)$$

$$R_p = K_p [M] \cdot \left(\frac{K_i}{K_t} \cdot f [I] \right)^{1/2} \quad \dots (11)$$

$$R_p = (K_p) \left(\frac{K_i}{K_t} \right)^{1/2} [M] [I]^{1/2}$$

$$R_p = K' [M] [I]^{1/2} \quad \dots (12)$$

This equation states that the rate of polymerisation is proportional to the first power of the concentration of the monomer and also to the square root of the concentration of initiator.

Degree of polymerisation

This is given by the symbol X_n or D_p and is defined as the number of the repeat units in a polymer chain. As such it is clearly related to chain length and the polymer molar mass \overline{M}_n . For example

$$\overline{X}_n = \frac{\overline{M}_n}{M_0}$$

where \overline{M}_n is equal to the number average relative molar mass (RMM) and M_0 is the monomer RMM. Since the propagation step (R_p) is the step which consumes monomer, and the termination step (R_t) is the step which leads to the production of polymer chain, then the number of units in a chain is given by the equation (12).



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$$\begin{aligned} \bar{X}_n &= \frac{R_p}{R_t} \\ \text{We know that } R_p &= K_p [M] \left(\frac{K_i}{K_t} \cdot f [I] \right)^{1/2} \quad \text{and} \quad R_t = R_i = 2f K_i [I] \\ \text{Therefore } \bar{X}_n &= \frac{K_p [M] \left(\frac{K_i}{K_t} \right)^{1/2} (f)^{1/2} (f)^{1/2}}{2f K_i [I]} \\ &= \frac{K_p}{2} [M] \cdot \frac{(K_i)^{1/2}}{K_i} \cdot \frac{(f)^{1/2}}{(f)} \cdot \frac{(f)^{1/2}}{[I]} \cdot \frac{1}{(K_t)^{1/2}} \\ &= \frac{K_p}{2} [M] \cdot \frac{1}{(K_i)^{1/2}} \cdot \frac{1}{(f)^{1/2}} \cdot \frac{1}{[I]^{1/2}} \cdot \frac{1}{(K_t)^{1/2}} \\ &= \frac{K_p \cdot [M]}{2 (K_i K_t)^{1/2} [I]^{1/2}} = K'' \frac{[M]}{[I]^{1/2}} \quad \dots (14) \end{aligned}$$

Thus we have two equations which characterises the effect of both monomers and initiator concentration on the polymerisation rate and resultant molar mass.

$$R_p = K' [M] [I]^{1/2} \quad \dots (12)$$

$$\bar{X}_n = K'' \frac{[M]}{[I]^{1/2}} \quad \dots (14)$$

$$\frac{M_n}{M_0} = \bar{X}_n = \frac{K'' [M]}{[I]^{1/2}} \quad \dots (15)$$

From these two equations the following may be deduced: (1) Rate will increase as both [M] and [I] increases (from equation 12). (2) RMM will decrease as [I] increases (equation 14). Varying both [M] and [I] is a means of controlling RMM (equation 15).

FACTOR AFFECTING CHAIN POLYMERISATION

Monomer Structure: Ethylene is the only monomer which polymerises well. under free radical mode of initiation. Propene and isobutene are unreactive under these conditions. Electron density at the double bond may determine whether a particular monomer polymerises by anionic, cationic or free radical mechanism (Table - 4).

Table 4. Susceptibility of monomers to type of initiation for chain polymerisation



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	Monomer structure	Electronic effect	Mode of initiation
(i)	$\text{CH}_2 = \text{CH} - \text{EDG}$	Inductive or resonance	Cationic, e.g., isobutene, vinyl ethers, styrene
(ii)	$\text{CH}_2 = \text{CH} - \text{EWG}$	Inductive or resonance	anionic, e.g., acrylonitrile, methyl methacrylate, styrene acrylic ester, vinylidene halide
(iii)	$\text{CH}_2 = \text{CH} - \text{G}$	—	Free radical, e.g., acrylonitrile, vinylacetate, vinyl chloride, styrene, $\text{CF}_2 = \text{CF}_2$.

C. CATIONIC POLYMERISATION

Structure and reactivity of monomers:

The active center in cationic polymerisation is a carbocation, and the monomer must therefore behave as a nucleophile in the propagation reaction. The most reactive vinyl monomers are those which have electron donating groups on the vinylic carbon. Any factor which increases the stability of carbocation also increases the reactivity of the monomer. For example the electron releasing inductive influence of alkyl groups causes isobutene to polymerise very quickly at low temperatures whereas propene reacts inefficiently and ethylene is particularly inert. For similar reasons, (X-methylstyrene is more reactive than the styrene. Substitution of an electron-donating group for an *ortho-or para* hydrogen increases monomer reactivity of styrene derivatives. Similarly electron-withdrawing group for an *ortho or para* hydrogen decreases monomer reactivity of styrene derivatives.

Conjugated olefines, like butadiene, 2-substituted butadiene and styrene, can be caused to polymerise by cationic and anionic as well as by free radical processes because the active site is delocalised in all cases. The most practical ionic polymerisations for these species are anionic, because such reactions involve fewer side reactions and better control of the diene polymer microstructure than in cationic systems. Free radical polymerisation of styrene is preferred over ionic processes for cost reasons.

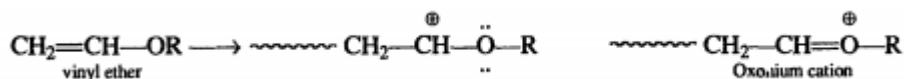
For efficient cationic polymerisation of vinyl monomers, it is necessary that the monomer should have electron-donating group bonded to vinylic carbon. Although vinyl acetate have an electron-donating group but it cannot be polymerised by cationic polymerisation because the carbonyl group complexes the active center. It is polymerised only by free radical mechanisms.

Other monomers that are suitable for cationic polymerisation include cyclic ethers, cyclic acetals, vinyl ethers and N-vinyl-carbazole. In these cases the heteroatom is directly



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bonded to cationic carbon and the respective carboxonium ion and immonium ion are more stable than the corresponding carbocations.



Because of high stability of onium ions, the monomers will not copolymerise cationically with olefins like isobutene or styrene.

Cationic polymerisations of vinyl monomers differ from other chain-growth polymerisation as follows:

- (1) Cationic polymerisations often involve complex initiation:
- (2) The reaction medium in cationic polymerisation is usually a polar chlorinated hydrocarbons like CHCl_3 ($\epsilon = 12.6$ at -20°C). Cationic polymerisations are characterised by extremely fast propagation rates.
- (3) The growth of vinyl polymer molecule in cationic reactions is limited by transfer rather than by true termination processes. Transfer of monomer is often the most important of these processes.
- (4) Some monomers isomerise during cationic polymerisations. The net result is that the structure of the polymer repeating unit is not the same as that of the monomer. This occurs if the carbocation which is formed by initial attack on the monomer can isomerise to a more stable form. Isomerisation is more common in cationic than in anionic or free radical polymerisation because carbocation rearrange easily.

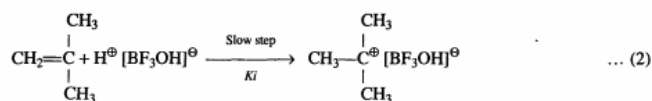
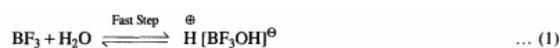
Kinetics of cationic polymerisation

Most of the cationic polymerisations proceed so rapidly that it is difficult to establish the steady state. However, the following kinetic scheme seems to be valid. Let us take the polymerisation of isopropene in the presence of BF_3 as lewis acid and H_2O as lewis base (*i.e.*, cocatalyst).

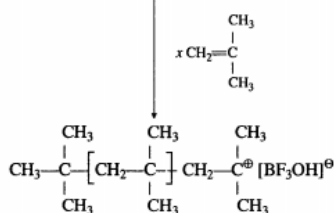
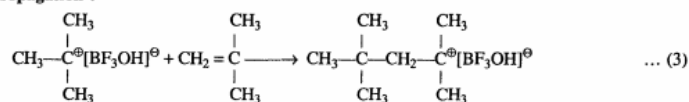


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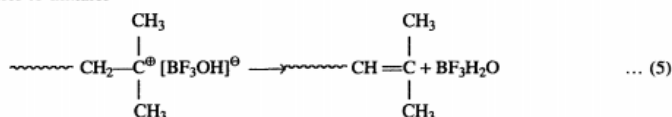


Propagation :

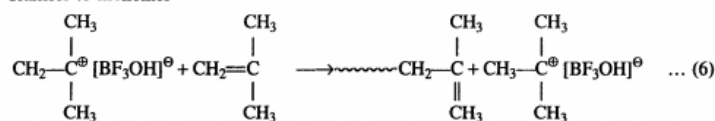


Termination and transfer

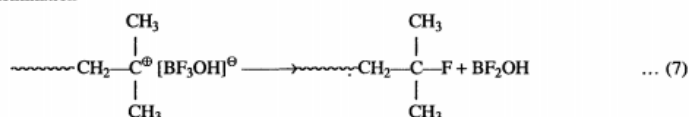
(i) Transfer to initiator



(ii) Transfer to monomer



(iii) Termination



The slow step in the initiation is given by equation (2). The initiation step (2) may be abbreviated and generalised as follows :



Here M stand for monomer. The kinetics of the initiation step is given by equation (8).

$$R_i = K_i [\text{M}] [\text{C}] \quad \dots (8)$$

where C is concentration of BF_3 , H_2O or $\text{H}^+ [\text{BF}_3\text{OH}]^-$. The propagation steps can be abbreviated and generalised as follows :





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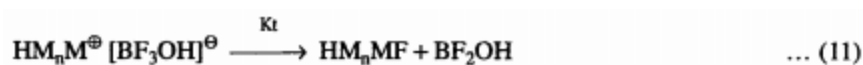
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Each reaction in the sequence involves the addition of a monomer to a monomer-ended cation, and each is assigned the same rate constant K_p on the reasonable assumption that the rate of addition reaction does not depend on the size of the participating macrocation.

Reaction (9c) is a bimolecular reaction and K_p is therefore, a second order rate constant. The rate of propagation is given by the equation (10).

$$R_p = K_p [\text{MH}^\oplus] [\text{M}] \quad \dots (10)$$

The termination of the chain can be abbreviated and generalised by the equation (11)



At this point it is interesting to note that unlike radical polymerisation, termination follows the first order kinetics (equation 12).

$$R_t = K_t [\text{MH}^\oplus] \quad \dots (12)$$

Applying the stationary rate (*i.e.*, $R_i = R_t$) gives equations (13) and (14).

$$R_i = R_t$$

$$K_i [\text{M}] [\text{C}] = R_t [\text{M}^\oplus\text{H}]^\oplus$$

$$[\text{MH}^\oplus] = \frac{K_i [\text{M}] [\text{C}]}{K_t} \quad \dots (13)$$

Putting the value of MH^\oplus in equation (10), we will get equation (14).

$$R_p = K_p [\text{MH}^\oplus] [\text{M}] \quad \dots (10)$$

$$= \frac{K_p \cdot K_i}{K_p} [\text{M}] [\text{C}] [\text{M}]$$

$$= \frac{K_p \cdot K_i}{K_p} [\text{M}]^2 [\text{C}] \quad \dots (14)$$

The degree of polymerisation of cationic polymerisation may be :

$$X_n = \frac{R_p}{K_t} = \frac{K_p [\text{M}]}{K_t} \quad \dots (15)$$

If termination by transfer to monomer is assumed, *i.e.*, $R_{tr} = K_{tr} [\text{MH}^\oplus] [\text{M}]$ then application of stationary state gives equations (16) and (17)

$$R_i = R_{tr}$$

$$K_i [\text{M}] [\text{C}] = K_{tr} [\text{MH}^\oplus] [\text{M}]$$

$$[\text{MH}^\oplus] = \frac{K_i [\text{C}]}{K_{tr}}$$

$$R_p = K_p [\text{MH}^\oplus] [\text{M}] \quad \dots (10)$$

$$= K_p \cdot \frac{K_i}{K_{tr}} [\text{C}] [\text{M}]$$

$$= \frac{K_p K_i}{K_{tr}} [\text{C}] [\text{M}]$$

$$= \frac{K_p K_i}{K_{tr}} [\text{M}] [\text{C}] \quad \dots (16)$$

$$X_n = \frac{R_p}{R_{tr}} \quad \dots (17)$$



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Equations (15) and (17) indicate that degree of polymerisation is independent of initiator concentration, and when chain transfer to monomer predominates, the degree of polymerisation is independent of monomer concentration also.

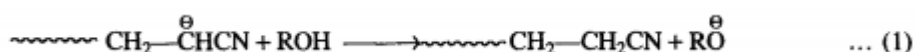
D. ANIONIC CHAIN POLYMERISATION

Anionic polymerisations are chain-growth processes in which the active centre is a negative ion which is associated with a positive counter ion. The degree of interaction between the macromolecular carbanion and its counterion depends on the nature of the respective ions and the medium in which polymerisation reaction is carried out.

Monomers that can be polymerised by anionic polymerisation include those in which carbanion is stabilised either by delocalisation of the negative charge or by the presence of an electron withdrawing group. Examples include styrene and butadiene, in which the carbon-carbon double bonds are conjugated and cyclic heteroatom compounds in which the negative charge can be delocalised onto atoms that are more electronegative than carbon. The latter group includes ethylene oxide, propylene sulphide and caprolactum. The examples of monomers having electron-withdrawing group includes vinylcyanide and nitro derivative of ethylene.

If the monomer contains reactive groups that could be attacked by carbanions (*i.e.*, base) they will not be suitable for anionic polymerisations. Halogen containing vinyl monomers are difficult to polymerise by anionic polymerisation because of the elimination of halides. Many initiators interact with carbonyl group of the monomers (acrylate monomers). In such cases polymerisation is carried out at very low temperature so that interaction between carbonyl group and initiator does not take place.

Anionic polymerisation is generally carried out in the presence of non-polar solvents with dielectric constants in the range of 2-10. Solvents polar protic solvents with high dielectric constants are generally not employed in anionic polymerisations. This is because these solvents are acidic enough to destroy carbanion active centers.



Polar aprotic solvents can also be not used because they may form strong complexes with carbanion and hinder addition reaction of monomers.



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The propagating carbanion and its counter ion exist as associated ion pairs in the presence of nonpolar solvents. In hydrocarbon solvents, ion pairs are not solvated but they may exist as aggregates.

Anionic chain growth polymerisations are distinguished from free radical polymerisations in the following respects :

(i) Initiation reaction is slow reaction in free radical polymerisations but very fast in anionic polymerisations. This facilitates the preparation of anionic polymers with narrow molecular weight.

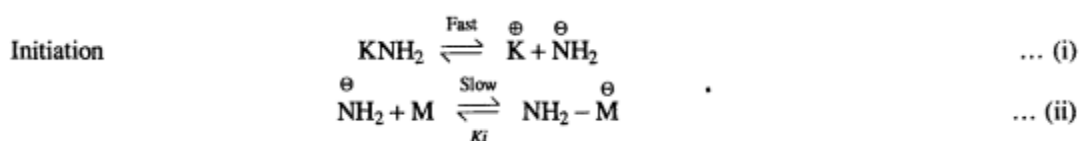
(ii) In anionic polymerisations only initiation and propagation steps are significant. Spontaneous termination reactions are effectively absent in number of anionic polymerisations. Macromolecular species in which the propagation reaction can be interrupted for lack of monomer and then resumed with same or a selected different monomer are called "Living polymers". Some block copolymers can therefore be produced by adding a second monomer to the living polymer.

(iii) The choice of initiator has no effect on the propagation reactions in free radical polymerisations but it can influence ionic propagations because the reactivity of the active center is partly determined by the nature of the counter ion that is derived from the initiator.

(iv) The choice of reaction medium is much more significant in anionic and cationic reactions than in free radical polymerisations because the character of the growing chain end is altered if the ion pair is more or less solvated.

Kinetics of anionic polymerisation

Most of the anionic polymerisation proceed so rapidly that it is difficult to establish the steady state. However, the following kinetic scheme seems to be valid for the anionic polymerisation initiated by KNH_2 . Initiation by KNH_2 was the first anionic polymerisation studied in greater detail.



Here M stand for monomer. The kinetics of the initiation is given by the equation (iii).

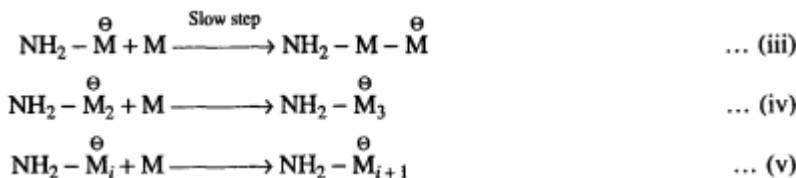


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$$R_i = K_i [M] [NH_2]^\ominus$$

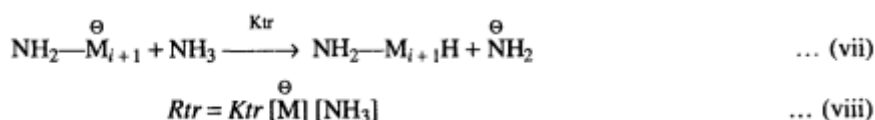
The propagation steps can be abbreviated and generalised as follows :



Each reaction in the sequence involves the addition of a monomer to a monomer-ended anion, and each is assigned the same rate constant K_p on the reasonable assumption that the rate of addition reaction does not depend on the size of the propagating macroanion. Reaction (iii) is a bimolecular reaction and K_p is therefore, a second order rate constant. The rate of propagation thus is given by the equation (vi).

$$R_p = K_p [M] [M]^\ominus \quad \dots \text{ (vi)}$$

Termination of the chain can be abbreviated and generalised by the equation (vii).



Applying the stationary rate (*i.e.*, $R_i = R_{tr}$) gives equations (ix) and (x)

$$\begin{aligned} R_i &= R_{tr} \\ K_i [M] [NH_2]^\ominus &= K_{tr} [M] [NH_3]^\ominus \\ [M]^\ominus &= \frac{K_i [M] [NH_2]^\ominus}{K_{tr} [NH_3]} && \dots \text{ (ix)} \end{aligned}$$

Putting the value of $[M]^\ominus$ in equation (vi), we will get the equation [X]

$$\begin{aligned} R_p &= K_p [M] [M]^\ominus && \dots \text{ (vi)} \\ R_p &= K_p [M] \frac{K_i [M] [NH_2]^\ominus}{K_{tr} [NH_3]} \\ R_p &= \frac{K_p K_i [M]^2 [NH_2]^\ominus}{K_{tr} [NH_3]} && \dots \text{ (x)} \end{aligned}$$

The degree of polymerisation of the anionic polymerisation is :

$$\bar{X}_n = \frac{R_p}{R_{tr}} = \frac{K_p [M]}{K_{tr} [NH_3]} \quad \dots \text{ (xi)}$$



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From the equation (xi) it is clear that by doubling the concentration of monomer leads to a doubling of the molar mass and a fourfold increase in the polymerisation rate.

E. COORDINATION POLYMERISATION

Free radical polymerisation of ethylene takes place at very high temperature (300 °C) and very high pressure (1000 atmosphere). Under this condition the resulting polymer have a highly branched backbone. This branched polymer have only moderate thermal and mechanical properties with limited crystallinity. This polymer is known as Low Density Polyethylene (LDPE).

In 1953 Ziegler found that polymerisation of ethylene took place at room temperature and atmospheric pressure in the presence of a catalyst. The product was a crystalline solid which was free from branching. The resulting linear polymer is now called High Density Polyethylene (HDPE).

When in 1954 Natta applied similar catalysts to the polymerisation of propene, a stereoregular isotactic polymer was obtained which was much tougher than free radical product. Thus Ziegler and Natta developed a catalyst system that polymerises alkenes to give linear polymers with high stereoselectivity. The catalysts systems are the mixture of transition metal halides (*e.g.*, titanium tetrachloride, vanadium oxychloride, molybdenum pentachloride, tungsten hexachloride etc.) and organometallic compounds (mostly trialkylaluminiums). The polymerisation of alkenes with metal halides activated by aluminium alkyls (Ziegler-Natta catalysis) is now one of the most important industrial processes. The catalysts are not soluble in the alkane solvents that are used for the polymerisations of alkenes. The reaction mixture is, therefore, a heterogeneous one, and polymerisation takes place at the surface of the catalyst.

The two components of the Zeigler-Natta catalyst are dissolved in a hydrocarbon solvent (toluene or n-heptane) at room temperature to give an exothermic reaction in which gases (butane, ethane, ethylene) are evolved and a dark-coloured solid, the catalyst, generally precipitates. The presence of butane, ethane ethylene, and short chain polyethylene is the catalyst mixture before the addition of the alkene monomer is due to the production of ethyl radicals. The reactions need care in the laboratory because of the reactivity of the reagents. For example, trialkylaluminium is pyrophoric (spontaneously inflammable with aerial



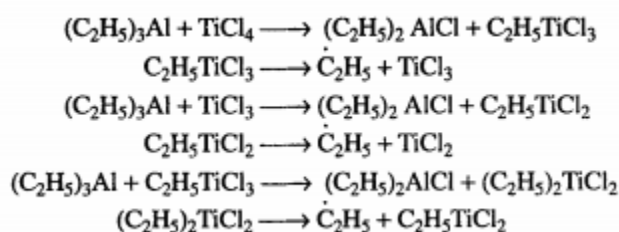
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oxygen), titanium tetrachloride spontaneously hydrolyses upon exposure to water vapour (in the air) and the alkene monomers are flammable.

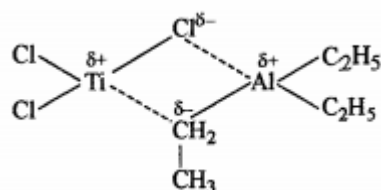
The important chemical step appears to be the reduction of titanium (IV) to lower valencies (**Scheme-I**). These are key reactive species because they can co-ordinate alkene double bonds, the first step in the polymerisation process when the monomer is exposed to the pre-prepared and aged catalyst. In general it is thought that polymerisation is a surface process which accounts for the stereochemical control.

There are a number of proposed mechanisms. The most acceptable mechanism is the bimetallic mechanism proposed by Natta (**Scheme-1**).



Scheme 1: Possible reactions during preparation of a co-ordination complex (Ziegler-Natta) catalyst from triethylaluminium and TiCl_4 .

It is generally supposed that the active component of the catalyst mixture is a complex formed between titanium trichloride and triethyl aluminium. The structure of this catalyst is as follows :

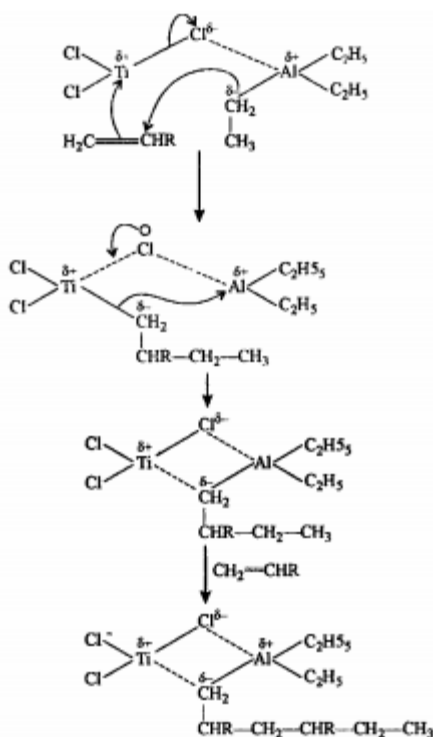


In this complex the titanium has unfilled 3d-orbitals to which may be co-ordinated π electrons from the double bond of the vinyl monomer. Thus a possible representation of initiation and propagation is as follows :



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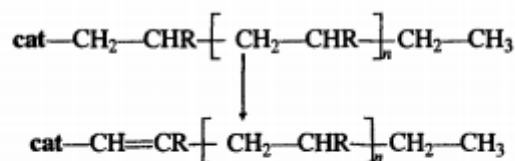
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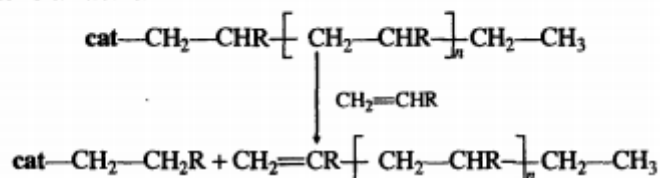
Scheme 2: Bimetallic mechanism for co-ordination complex catalysis of chain polymerisation.

The essential feature of this mechanism is that monomers are inserted, one after the other, into a polarised titanium-carbon bond. The polymer therefore, grows out of the active centre, rather as a hair grows from the root. It will be noticed that the propagating end of the polymer chain is negatively charged and therefore the reaction may be regarded as an anionic polymerisation. Chain growth may be terminated by several types of transfer, *e.g.*,

Internal hydride transfer :



Transfer to monomer :

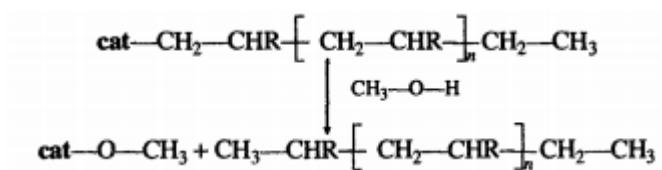


True (kinetic) termination may be brought about by the addition of an active hydrogen compound such as an alcohol :



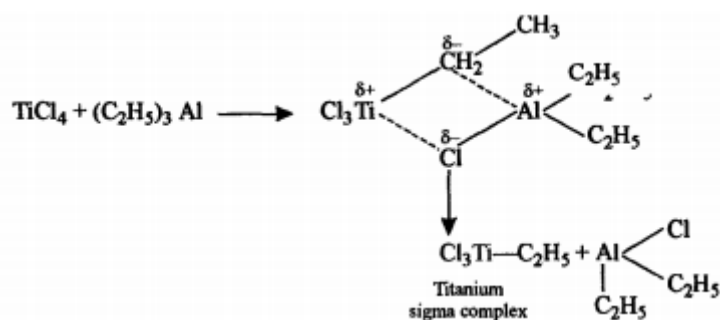
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The mono metallic mechanism is given by Cossee-Arlman which is given in **scheme 1**.

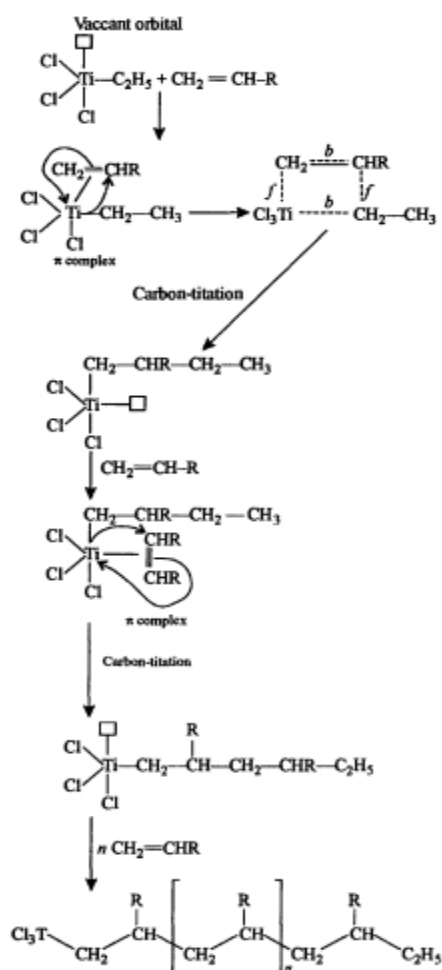
According to this mechanism TiCl_4 reacts with triethyl aluminium to form a titanium sigma complex which is the true catalyst for the polymerisation.



The alkyl-Ti sigma complex can form a π -complex with the first molecule of alkene and then carry out a carbo-titration of the π -bond. This establishes the first carbon-carbon bond.

Insertion of the next alkene by a repeat of the previous step now starts the polymerisation. Each new carbon-carbon bond is formed on the coordination sphere of the Ti atom by transformation of a π -complex into σ -complex. Repetition of this process leads to polymerisation (**Scheme-3**).

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Scheme-3

According to the mechanism the alkene is coordinated to the transition metal through overlap of the alkene π electrons with the vacant d orbitals of the metal. The bond between the transition metal and the ethyl group is weakened by this coordination and propagation takes place by insertion of the complexed alkene between the metal and ethyl group *via* a four membered cyclic transition state. The unsubstituted carbon atom of the alkene becomes attached to the metal during the opening of the double bond, which is always a *cis* addition.

In the mechanism, insertion of a monomer results in an interchange of the polymer substituent and the lattice vacancy. These are not equivalent positions in the crystal lattice of the crystal. Under normal polymerisation conditions, the macromolecular alkyl group appears to shift back to its original position before next monomer is added. This leads the formation of isotactic polymers.



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However, if the polymer chain and the vacant orbital were to exchange (as shown in the mechanism) initial positions, then the placements of successive monomers would alternate stereochemically. This provides syndiotactic polymers.

Table 2. shows how the choice of catalyst can influence the stereo regularity of the polymer.

Table 2: Effect of coordination complex catalyst upon stereo regularity of polypropen

Catalyst	Stereo regularity (%)
$(C_2H_5)_3Al + TiCl_4$	35
$(C_2H_5)_3Al + TiCl_4 + NaF$	97
$(C_2H_5)_3Al + TiCl_3$	85
$(C_2H_5)_2AlCl + TiCl_3$	99

In polymerisation of this type, each monomer is inserted between the growing macromolecule and the metal (*i.e.*, initiator), complexing of the monomer to the initiator proceeds the insertion process and this polymerisation is therefore often called coordination polymerisation.

F. POLYMERIZATION CONDITIONS

Table 3. Comparison of Polymerization Systems

Type	Advantages	Disadvantages
Homogeneous		
Bulk (batch type)	Minimum contamination. Simple equipment for making castings.	Strongly exothermic. Broadened molecular-weight distribution at high conversion. Complex if small particles required.
Bulk (continuous)	Lower conversion per pass leads to better heat control and narrower molecular-weight distribution.	Requires agitation, material transfer, separation, and recycling.
Solution	Ready control of heat of polymerization. Solution may be directly usable.	Not useful for dry polymer because of difficulty of complete solvent removal.
Heterogeneous		
Suspension	Ready control of heat of polymerization. Suspension or resulting granular polymer may be directly usable.	Continuous agitation required. Contamination by stabilizer possible. Washing, drying, possibly compacting required.
Emulsion	Rapid polymerization to high molecular weight and narrow distribution, with ready heat control. Emulsion may be directly usable.	Contamination with emulsifier, etc., almost inevitable, leading to poor color and color stability. Washing, drying, and compacting may be required.

POLYMERIZATION IN HOMOGENEOUS SYSTEM



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Bulk Polymerization.

Polymerization in bulk, perhaps the most obvious method of synthesis of polymers, is widely practiced in the manufacture of condensation polymers, where the reactions are only mildly exothermic, and most of the reaction occurs when the viscosity of the mixture is still low enough to allow ready mixing, heat transfer, and bubble elimination. Control of such polymerizations is relatively easy.

Bulk polymerization of vinyl monomers is more difficult, since the reactions are highly exothermic and, with the usual thermally decomposed initiators, proceed at a rate that is strongly dependent on temperature. This, coupled with the problem in heat transfer incurred because viscosity increases early in the reaction, leads to difficulty in control and a tendency to the development of localized "hot spots" and "runaways". Except in the preparation of castings, for example, of poly(methyl methacrylate), bulk polymerization is seldom used commercially for the manufacture of vinyl polymers.

Solution Polymerization.

Polymerization of vinyl monomers in solution is advantageous from the standpoint of heat removal (e.g., by allowing the solvent to reflux) and control, but has two potential disadvantages. First, the solvent must be selected with care to avoid chain transfer and, second, the polymer should preferably be utilized in solution, as in the case of poly(vinyl acetate) to be converted to poly(vinyl alcohol) and some acrylic ester finishes, since the complete removal of solvent from a polymer is often difficult to the point of impracticality.

POLYMERIZATION IN HETEROGENEOUS SYSTEM

Polymerization From Gaseous Monomers

The polymerization of gaseous monomers can take place with the formation of a liquid phase (polymer melt) or a solid polymer. In each case the polymerization of ethylene provides the most important industrial example.

The high-pressure polymerization of ethylene to branched polyethylene takes place by a free-radical mechanism in the presence of a liquid phase, at temperatures above the melting point of the polymer. The polymerization is carried only to low conversion, with the remaining ethylene recovered when the pressure is lowered and recycled.



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The low-pressure polymerization of ethylene to linear polyethylene takes place by coordination polymerization using a catalyst suspended in gaseous ethylene in a fluid-bed reactor. The ethylene polymerizes to the solid phase, with the small amount of the catalyst required remaining in the solid polymer.

Emulsion Polymerization

In emulsion polymerization two immiscible liquid phases are present, an aqueous continuous phase and a nonaqueous discontinuous phase consisting of monomer and polymer, as described below. The initiator is located in the aqueous phase, and the monomer-polymer particles are quite small, of the order of $0.1 \mu\text{m}$ in diameter. The kinetics of emulsion polymerization differs importantly from that of bulk polymerization.

Other Heterogeneous Liquid Systems

Suspension Polymerization.

The term *suspension polymerization* refers to polymerization in an aqueous system with monomer as a dispersed phase, resulting in polymer as a dispersed solid phase. The process is distinguished from superficially similar emulsion polymerization by the location of the initiator and the kinetics obeyed: In typical suspension polymerization the initiator is dissolved in the monomer phase, and the kinetics is the same as that of bulk polymerization.

The dispersion of monomer into droplets much larger than those found in emulsion polymerization, typically $0.01\text{-}0.5 \text{ cm}$ in diameter, is maintained by a combination of agitation and the use of water-soluble stabilizers. These may include finely divided insoluble organic or inorganic materials that interfere with agglomeration mechanically, electrolytes to increase the interfacial tension between the phases, and water-soluble polymers to increase the viscosity of the aqueous phase

Precipitation Polymerization.

In the preparation of a polymer insoluble in its monomer, or in polymerization in the presence of a nonsolvent for the polymer, marked deviations from the kinetics of



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homogeneous radical polymerization may occur. The normal bimolecular termination reaction is not effective, as the result of trapping or occlusion of radicals in the unswollen, tightly coiled precipitating polymer. The theory has been confirmed by the demonstration of the presence of radicals in the polymer both by chemical methods and by electron paramagnetic resonance. The lifetime of the trapped radicals is many hours at room temperature, and if polymer containing such radicals is heated in the presence of monomer to a temperature where the mobility of the radicals is increased, extremely rapid polymerization takes place.

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Acknowledgement: Special thanks to Dr. Soumendu Bisoi for his contribution.