Polymer Chemistry

Macromolecules

Macro molecules also known as polymers, consist of a large no. of simple monomeric structural unit which reapeated over and over again to form a giant like molecule by the covalent linkage b/w the reapiting repeating monomers.

for example in the polymer —A—A—A—A—A— and —A-B-A-B-A-B— for instance, the repeate units are A and A—B respectirey

e.g. Poly ethylene

$$m\ CH_2 = CH_2 \longrightarrow \{CH_2 - CH_2\}_n$$

Degree of polymerisation

The degree of polymerisation represents the no. of structural or monomeric units contained in a polymer. It is generally represent by K or DPari

$$K = \frac{M_P}{M_o}$$

M_P = mass of Polymer

M_o = " " monomer

Extent of polymerisation

It is the fraction of monomer reacted at a given time i.e. it is the ratio of no. of molecules undergoing reac^n to the intial no. of molecules. It is denoted by P.

So, $$P = \frac{N_o - N}{N_o}$$

$$\Rightarrow P = 1 - \frac{N}{N_o}$$

$$\Rightarrow \frac{N_o}{N} = \frac{1}{1-P}$$

N_o = no. of total monomer / initial no. of molecules

N = no of monomer at a given time / The no. of molecules which does not undergoing reac^n.

Molar masses of Polymers

The molar mass of a polymer increases continuously during the condensation reaction involved depending upon the degree of polymerisation. However, since the polymerisation chains might be broken at different stages, the final pdt generally contains macromolecules of different masses. It is necessary, therefore to taken an avg. molar masses in these substances. To describe the distribution of molar masses, the following avg. are commonly used.

i) Number avg. molar mass ($\overline{M_n}$)

It is defined as the obtained by carrying out the summation over the fraction of molecules multiplied by their corresponding molar mas. i.e.

$$\overline{M_n} = \sum_i f_i M_i$$

Subscript n stands for no. and f is as

$$f_i = \frac{N_i}{N_{total}}$$

Where N_i is the no. of molecules each having molar mass M_i and N_{total} is the total no. of molecules given by

$$N_{total} = \sum_i N_i$$

So, $$\overline{M_n} = \frac{\sum_i N_i M_i}{\sum_i N_i}$$; N_i = no. of i type molecule per unit vol^n

$$= \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \cdots}{N_1 + N_2 + N_3 + \cdots}$$

ii) Mass avg. molar mass ($\overline{M_m}$)

Obtained by the carrying out summation over the fraction by their corresponding molar mass, i.e.

$$\overline{M_m} = \sum_i w_i M_i$$; it also given by symbol $\overline{M_w}$

$\overline{M_w}$ = Weight avg. molar mass

Where $$w_i = \frac{m_i}{m_{total}}$$

Where m_i is the mass of the polymer molecules, each having molar mass M_i and m_{total} is the total mass of the sample as

$$m_{total} = \sum_i m_i$$

Thus,
$$\overline{M_m} = \frac{\sum_i m_i \cdot M_i}{\sum m_i}$$

Again $m_i = \frac{N_i}{N_A} \cdot M_i$ [since m_i is the mass per unit vol^m it may be taken as c_i]

So, $\overline{M_m} = \frac{\sum_i N_i M_i^2}{\sum N_i \cdot M_i}$

$$= \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 + \cdots}{N_1 M_1 + N_2 M_2 + N_3 M_3 + \cdots}$$

We can also write

$$\overline{M_m} = \frac{\sum_i c_i M_i}{\sum_i c_i}$$

and $\overline{M_n} = \frac{\sum_i c_i}{\sum_i (c_i/M_i)}$

$$\left\{ \begin{array}{l} \overline{M_n} = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i m_i N_A}{\sum_i \frac{m_i N_A}{M_i}} \\[3mm] = \frac{\sum_i c_i}{\sum_i (c_i/m_i)} \end{array} \right.$$

iii) Z-avg. molar mass ($\overline{M_z}$)

It is related as third power of avg. molecular weight in a polydisperse prlymer

i.e. $\overline{M_z} = \dfrac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}$

Generally $\overline{M_z} > \overline{M_m} > \overline{M_n}$

iv) Viscosity avg. molar mass ($\overline{M_v}$)

The viscosity avg. molar mass is defined as

$$\overline{M_v} = \left(\frac{\sum_i N_i M_i^{(a+1)}}{\sum_i N_i \cdot M_i} \right)^{1/a}$$

$$\Rightarrow \left(\overline{M_v} \right)^a = \frac{\sum_i N_i M_i^{(a+1)}}{\sum_i N_i M_i} = \frac{\sum_i c_i M_i^a}{\sum_i c_i}$$

Where a is characterised by the system under investigation and generally lies in the range $0.5 < a \leq 1.0$

Note, $\overline{M_v} = \overline{M_m}$ for $a = 1$.

Q.4 Show that $\overline{M_m} \geqslant \overline{M_n}$

Ans

$$\overline{M_m} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad \text{and} \quad \overline{M_n} = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

Now, $\overline{M_m} - \overline{M_n} = \dfrac{\sum_i N_i M_i^2}{\sum_i N_i M_i} - \dfrac{\sum_i N_i M_i}{\sum_i N_i}$

$$= \frac{\left\{ \sum_i N_i \cdot \sum_i N_i M_i^2 - \left(\sum_i N_i M_i \right)^2 \right\} \times \frac{1}{\sum_i N_i^2}}{\left\{ \sum_i N_i \cdot \sum_i N_i M_i \right\} \cdot \frac{1}{\sum_i N_i^2}}$$

$$= \frac{\dfrac{\sum_i N_i M_i^2}{\sum_i N_i} - \left(\dfrac{\sum_i N_i M_i}{\sum_i N_i} \right)^2}{\dfrac{\sum_i N_i M_i}{\sum_i N_i}}$$

$$= \frac{\overline{M_n^2} - \overline{M_n}^2}{\overline{M_n}}$$

Now, $\left(M_i - \overline{M_n} \right)^2 \geqslant 0$

$\Rightarrow M_i^2 - 2 M_i \overline{M_n} + \overline{M_n}^2 \geqslant 0$

$\Rightarrow \overline{M_n^2} - 2 \overline{M_n}^2 + \overline{M_n}^2 (\geqslant 0)$ [for i becoming n^{th} constitent]

$\Rightarrow \overline{M_n^2} - \overline{M_n}^2 \geqslant 0$

So, $\dfrac{\overline{M_n^2} - \overline{M_n}^2}{\overline{M_n}} \geqslant 0$

$\Rightarrow \overline{M_m} - \overline{M_n} \geqslant 0$

$\Rightarrow \overline{M_m} \geqslant \overline{M_n}$

Proved

Distribution of molecular sizes

Let us take a generalize polymerisation as

$$A_1 + A_1 \xrightarrow[\text{step}]{1^{st}} A_2$$

$$A_1 + A_2 \xrightarrow[\text{step}]{2^{nd}} A_3$$

$$A_1 + A_3 \xrightarrow[\text{step}]{3^{rd}} A_4$$

$$\vdots \qquad \vdots$$

$$A_1 + A_{i-1} \xrightarrow[\text{Step}]{(k-1)^{th}} A_k$$
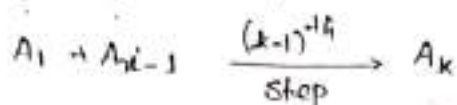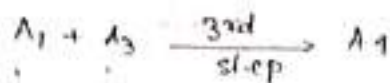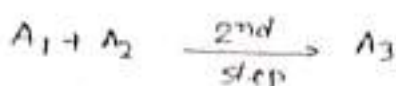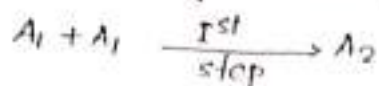
Probability of finding a polymer with size 'k' is equal to the probability of having $(k-1)$ elementary step in polymerisation processes. i.e in a k-mer, there are $(k-1)$ no. of group A reacted.

Now probability of each step is equal because

i) The reac^n does not depend on the chain length and.

ii) Conc. of monomer is very big large.

Thus Probability of k-mer is given by

$$\pi_k \propto p^{(k-1)} \qquad ; P = \text{extent of polymerisation}$$

$$\Rightarrow \pi_k = c p^{(k-1)} \qquad ; c = \text{Proportionality con}^t.$$

$$\Rightarrow \sum_{k=1}^{\infty} \pi_k = c \sum_i p^{(k-1)}$$

$$\Rightarrow 1 = c \left[1 + p^2 + p^3 + \cdots \right]$$

$$\Rightarrow 1 = c (1-P)^{-1}$$

$$\Rightarrow c = (1-P)$$

Since series $(1+P^2+P^3+\cdots)$ gives $(1-P)^{-1}$

So, $\pi_k = (1-P) p^{(k-1)}$

Let us calculate $\overline{M_n}$ and $\overline{M_m}$ in terms of P

$$\overline{M_n} = \sum_i \left(\frac{N_i}{N}\right) M_i = \sum_i \pi_i \cdot M_i$$

$$= \sum_i (1-P) p^{(i-1)} \cdot M_i = \sum_i (1-P) \cdot p^{(i-1)} \cdot i M_0$$

$$= (1-P) M_0 \sum_i i \, p^{(i-1)}$$

$$= (1-P) M_0 \left[1 + 2P + 3P^2 + \cdots \right]$$

$$= (1-P) M_0 \cdot \frac{1}{(1-P)^2}$$

$$\Rightarrow \overline{M_n} = \frac{M_0}{(1-P)} \qquad \Rightarrow \frac{\overline{M_n}}{M_0} = \frac{1}{(1-P)}$$

$i = \frac{M_i}{M_0}$; $M_0 = \text{mass of monomer}$

$(1 + 2P + 3P^2 + \cdots) = (1-P)^{-2}$

so, no. avg. extent of Polymerization ($\overline{X}_n$) is given as

$$\overline{X}_n = \frac{\overline{M}_n}{M_n} = \frac{1}{(1-P)}$$

$$\begin{cases} \sum\limits_{k=0}^{\infty} P^k = 1 + P + P^2 + \cdots = \frac{1}{1-P} \\ \\ \Rightarrow \sum\limits_{k=1}^{\infty} k P^{(k-1)} = -\frac{1}{(1-P)^2} \cdot (-1) = \frac{1}{(1-P)^2} \end{cases}$$

Now, we have

$$\overline{M}_m = \sum_i w_i M_i \longrightarrow (1)$$

Also, $\overline{M}_m = \dfrac{\sum\limits_i N_i M_i^2}{\sum\limits_i N_i M_i} = \dfrac{\sum\limits_i \left(\frac{N_i}{N_0}\right) M_i^2}{\sum\limits_i \left(\frac{N_i}{N_0}\right) M_i}$

$$= \frac{\sum\limits_i \pi_i M_i^2}{\sum\limits_i \pi_i M_i} = \frac{\sum\limits_i \pi_i \cdot i M_0 \cdot M_i}{\sum\limits_i \pi_i \, i M_0}$$

$$= \frac{\sum\limits_i i \, \pi_i M_i}{\sum\limits_i i \, \pi_i} \longrightarrow (2)$$

Comparing eqn (1) and (2) we get

$$w_i = \frac{i \, \pi_i}{\sum\limits_i i \, \pi_i}$$

$$= \frac{i (1-P) \cdot P^{(i-1)}}{\sum\limits_i i (1-P) P^{(i-1)}} = \frac{i P^{(i-1)}}{\sum\limits_i i P^{(i-1)}}$$

$$\Rightarrow w_i = i P^{(i-1)} \cdot (1-P)^2$$

So, $\overline{M}_m = \sum\limits_i w_i M_i = \sum\limits_i i (1-P)^2 P^{(i-1)} M_i$

$$= (1-P)^2 \sum\limits_i i \cdot P^{(i-1)} \cdot i M_0$$

$$= (1-P)^2 M_0 \sum\limits_i i^2 P^{(i-1)} \longrightarrow (3)$$

Let evaluate $\sum\limits_i i^2 P^{(i-1)}$

we have already
$$\sum_i i \cdot p^{(i-1)} = \frac{1}{(1-P)^2}$$

$$\Rightarrow \sum_i i \cdot p^i = \frac{P}{(1-P)^2} \quad \left[\text{multiplying both sides by } P\right]$$

Now differentiating both sides we have

$$\sum_i i^2 p^{(i-1)} = \frac{1}{(1-P)^2} + \frac{-P}{(1-P)^3} \times (-1)$$

$$= \frac{1-P+2P}{(1-P)^3} = \frac{1+P}{(1-P)^3}$$

Therefor eq^n (3) becomes

$$\overline{M_m} = (1-P)^2 \cdot M_o \cdot \frac{1+P}{(1-P)^3}$$

$$= \frac{1+P}{1-P} M_o$$

$$\Rightarrow \frac{\overline{M_m}}{M_o} = \frac{1+P}{1-P}$$

$$\Rightarrow \overline{M_m} = (1+P)\overline{M_n}$$

$$\Rightarrow \frac{\overline{M_m}}{\overline{M_n}} = (1+P)$$

$$\left[\begin{array}{l} \overline{M_n} = \frac{M_o}{(1-P)} \\[2mm] \frac{\overline{M_m}}{\overline{M_n}} = \text{Polydispersy index} \end{array}\right]$$

We have mass fraction or weight fraction of polymer (W_i) as

$$W_i = i(1-P)^2 p^{(i-1)}$$
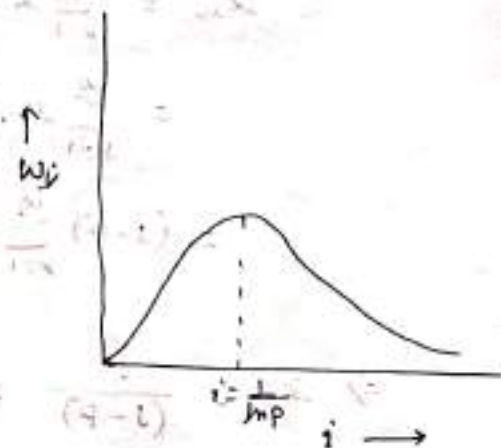
$$\Rightarrow \ln W_i = \ln i + 2\ln(1-P) + (i-1)\ln P$$

$$\Rightarrow \frac{d\ln W_i}{di} = \frac{1}{i} + \ln P$$

$$\Rightarrow \frac{1}{W_i}\frac{dW_i}{di} = \frac{1}{i} + \ln P$$

$$\Rightarrow \frac{d^2 \ln W_i}{di} = -\frac{1}{i^2} < 0 \quad \text{i.e. maxima}$$

setting $\frac{dW_i}{di}$ as zero we get

$$i'_{max} = \frac{1}{\ln P}$$

Now
$$w_i = i(1-P)^2 \, P^{(i-1)}$$

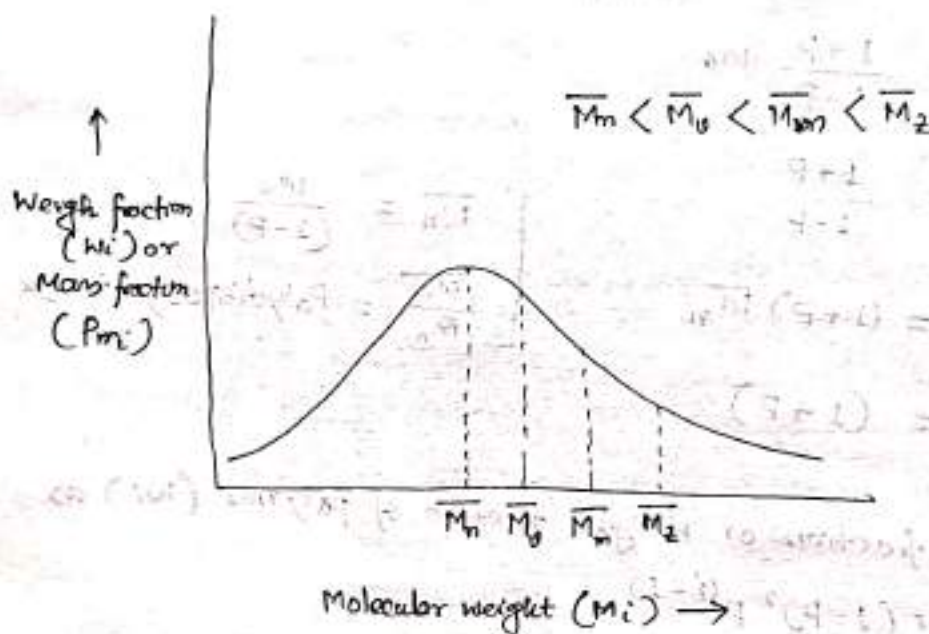$$P_{m_i} = M_0 \, w_i = M_0 (1-P)^2 \, i \, P^{(i-1)}$$

$$= (1-P)^2 \, M_i \, P^{i-1}$$

$$= (1-P)^2 \, M_i \, P^{\left(\frac{M_i}{M_0} - 1\right)}$$

$$\Rightarrow \ln P_{m_i} = 2\ln(1-P) + \ln M_i + \left(\frac{M_i}{M_0} - 1\right)\ln P$$

$$\Rightarrow \frac{d\ln P_{m_i}}{dM_i} = \frac{1}{M_i} + \frac{1}{M_0}\ln P$$

$$\Rightarrow \frac{d^2 \ln P_{m_i}}{dM_i} = -\frac{1}{M_i^2} < 0$$

$$\overline{M_n} < \overline{M_v} < \overline{M_m} < \overline{M_z}$$

Weight fraction (w_i) or Mass fraction (P_{m_i}) — vertical axis

$\overline{M_n} \; \overline{M_v} \; \overline{M_m} \; \overline{M_z}$

Molecular weight $(M_i) \longrightarrow$

Avg. degree of polymerization (k_{av})

Avg. value of k is defined as

$$k_{av} = \sum_{k=1}^{\infty} k\, \Pi_k$$

$$= \sum_{k=1}^{\infty} k \cdot (1-P)\, P^{(k-1)}$$

$$= (1-P)\sum_{k=1}^{\infty} k \cdot P^{(k-1)} = \frac{1-P}{(1-P)^2}$$

$$\Rightarrow k_{av} = \frac{1}{(1-P)} = \frac{M_P}{M_0}$$

Q) Define Poly dispersity index and hence show that $\overline{M_m} \geqslant \overline{M_n}$

Ans: The ratio $\dfrac{\overline{M_m}}{\overline{M_n}}$ is a measure of the polydispersity of a sample of a polymer. i.e.

$$\text{Polydispersity} = \dfrac{\overline{M_m}}{\overline{M_n}} = (1+P)$$

where P = extent of polymerisation

$$\overline{M_m} = \dfrac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad \text{and} \quad \overline{M_n} = \dfrac{\sum_i N_i M_i}{\sum_i N_i}$$

For monodisperse sample, $P=0$

then $\dfrac{\overline{M_m}}{\overline{M_n}} = 1 \Rightarrow \overline{M_m} = \overline{M_n}$

For poly disperse sample $P > 0$, then

$$\dfrac{\overline{M_m}}{\overline{M_n}} > 1 \Rightarrow \overline{M_m} > \overline{M_n}$$

Combining we get $\overline{M_m} \geqslant \overline{M_n}$

__Proved.__

Q) A hydroxyacid $HO \{CH_2\}_5 COOH$ is polymerised and is found that the pdt has a no. avg. molar mass 20000 g/mol.
i) What is extent of reaction   ii) What is the degree of polymerisation
iii) Find the mass avg. molar mass?

Ans:
i) We have $\overline{M_n} = \dfrac{M_o}{1-P}$

$$\Rightarrow P = 1 - \dfrac{M_o}{\overline{M_n}} = 1 - \dfrac{132}{20000}$$

$$= 1 - 0.0066 = 0.9934$$

ii) $x_{av} = \dfrac{1}{(1-P)} = \dfrac{1}{1-0.9934} = 151.5$

$x_{av} = \dfrac{\overline{M_n}}{M_o} = \dfrac{20000}{132} = 151.5$

iii) $\overline{M_m} = \overline{M_o}(1+P)$

$= 20000 (1+0.9934)\, g/mol$

$= 39868 \, g/mol$

Q] A solution contains equal no of particles with molar masses 10000 g/mol and 20000 g/mol respectively. Calculate $\overline{M_n}$ and $\overline{M_m}$.

Ans

$$\overline{M_n} = \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2}$$

Since $N_1 = N_2$, we get

$$\overline{M_n} = \frac{M_1 + M_2}{2} = \frac{10000 + 20000}{2} \, g/mol = 15000 \, g/mol$$

Again $\overline{M_m} = \frac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_2 M_2}$

$$= \frac{M_1^2 + M_2^2}{M_1 + M_2} \qquad [\because N_1 = N_2]$$

$$= \frac{(10000)^2 + (20000)^2}{10000 + 20000} \, g/mol = 16666 \cdot 6 \, g/mol$$

Q] A suspension contains equal masses of particles with molar masses 10000 g/mol and 20000 g/mol respectively. Calculate $\overline{M_n}$ and $\overline{M_m}$.

Ans

Since, $m = \frac{N}{N_A} \cdot M$, so, $N = \left(\frac{m}{M}\right) N_A$

$$\overline{M_n} = \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2} = \frac{\frac{m_1}{M_1} N_A M_1 + \frac{m_2}{M_2} N_A M_2}{\left(\frac{m_1}{M_1}\right) N_A + \left(\frac{m_2}{M_2}\right) N_A}$$

$$= \frac{m_1 + m_2}{\frac{m_1}{M_1} + \frac{m_2}{M_2}} = \frac{2 m_1}{m_1 \left(\frac{1}{M_1} + \frac{1}{M_2}\right)} \qquad [\because m_1 = m_2]$$

$$= \frac{2 M_1 M_2}{M_1 + M_2} = \frac{2 \times 10000 \times 20000}{10000 + 20000} \, g/mol = 13333 \cdot 3 \, g/mol.$$

Again, $\overline{M_m} = \frac{N_1 M_1^2 + N_2 M_2^2}{N_1 M_1 + N_1 M_1} = \frac{N_A m_1 M_1 + N_A m_2 M_2}{N_A m_1 + N_A m_2}$

$$= \frac{m_1 M_1 + m_2 M_2}{m_1 + m_2} = \frac{m(M_1 + M_2)}{2 m_1} \qquad [\because m_1 = m_2]$$

$$= \frac{M_1 + M_2}{2} = \frac{10000 + 20000}{2} \, g/mol$$

$$= 15000 \, g/mol$$

Molecular weight determination

i) Osmometry
ii) Viscometry
iii) Light scattering
iv) End-group analysis
v) Sedimentation, etc.

Osmometry

The no. avg. molar mass of many polymer can be measured conveniently by osmometry. Using the colligative nature of osmotic pressure, the value of $\overline{M}_n$ is determined.

From thermodynamic derivation of osmotic pressure (π) we have

$$\pi V = nRT = \frac{c}{M} \cancel{V} RT \quad \Rightarrow \quad \pi = \frac{c}{M} RT$$

$V = $ vol^m of sol^m, $T = $ temp of experiment

$n = $ no. of moles of species.

The above eq^n is strictly valid for ideal and monodisperse sol^n only. Since polymer is a non-ideal sol^n and also poly disperse. So, it will not directly applicable for polymer sol^n.

Thus, with the introduction of non-ideality π may be written as

$$\pi = \frac{c}{M} RT + b(T) \cdot RT \left(\frac{c}{M}\right)^2 + \cdots \longrightarrow (1)$$

For ideal sol^n $b(T) = 0$

Now $c = \dfrac{m}{V} = N$

Now, $\dfrac{c}{M} = \dfrac{n}{V} = \dfrac{m}{VM}$

$$= \frac{N}{N_A V} \quad \Rightarrow \quad c = \frac{NM}{N_A V} \longrightarrow (2)$$

Thus rearranging we get

$$\pi = \frac{N}{N_A V} RT + b(T) \cdot RT \cdot \left(\frac{N}{N_A V}\right)^2 + \cdots \longrightarrow (3)$$

Again from eq^n (2) we have

$$c = \frac{NM}{N_A V}$$

i.e. $c_1 = \dfrac{N_1 M_1}{N_A V}$, $c_2 = \dfrac{N_2 M_2}{N_A V}$, $\cdots$ $c_i = \dfrac{N_i M_i}{N_A V}$ and so on.

Thus introducing polydispersy here we have

$$c = \sum_i c_i$$

$$= \frac{\sum_i N_i \cdot M_i}{N_A V} = \frac{\frac{\sum_i N_i M_i}{\sum_i N_i} \cdot \sum_i N_i}{N_A V}$$

$$= \frac{M_n \cdot N}{N_A \cdot V}$$

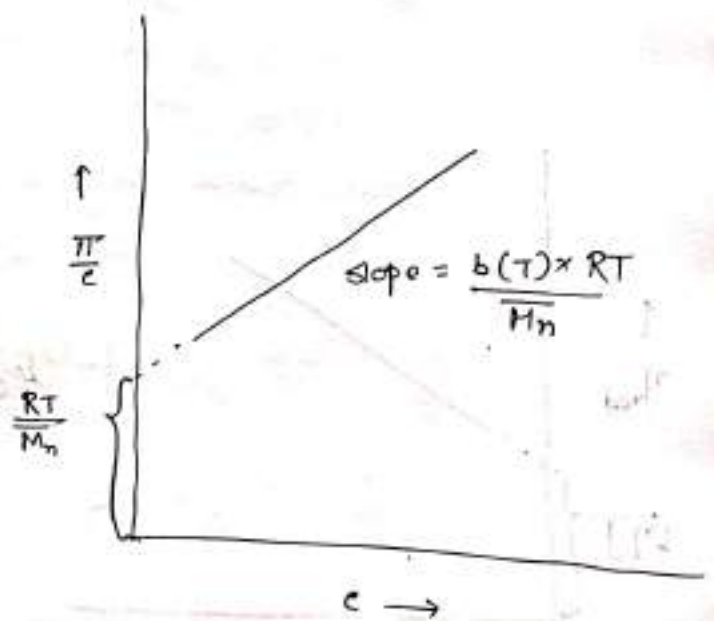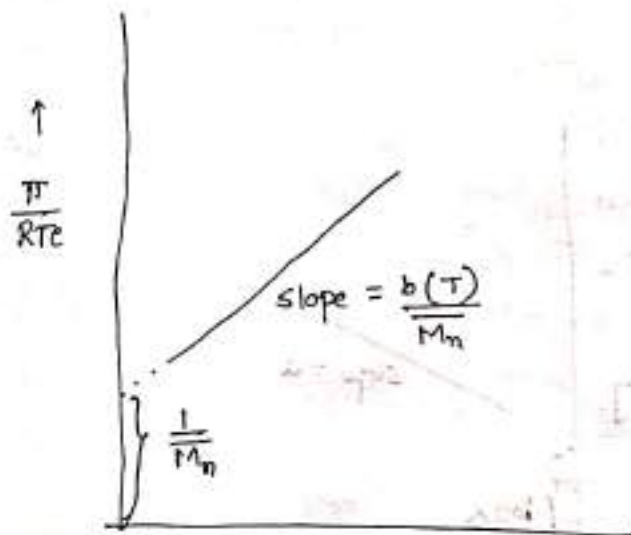$$\Rightarrow \frac{c}{M_n} = \frac{N}{N_A V} \longrightarrow (4)$$

substitute (4) in eqn (3) we may write

$$\pi = \frac{c}{M_n} RT + b(T) \left(\frac{c}{M_n}\right)^2 RT + \cdots$$

$$\Rightarrow \frac{\pi}{cRT} = \frac{1}{M_n} + b(T) \cdot \frac{c}{M_n} \quad \{neglect\; all\; the\; higher\; terms\}$$

$$\Rightarrow \frac{\pi}{c} = \frac{RT}{M_n} + b(T) \cdot \frac{RTc}{M_n}$$

The above eqn are applicable for polymer sol^n.

Viscometry

The most evident distinguish property of a polymer sol^n is its viscosity. The measurement provide viscosity avg. molar mass $(\overline{M}_v)$. Determination of $\overline{M}_v$ requires the measurement of the viscosity of a polymer sol^n relative to that of the pure solvent.

The intrinsic viscosity of a polymer sol^n is found to increase with increase in avg. molar mass of polymer $(\overline{M}_v)$.

This is given by Mark-Houwink eq^n as

$$[\eta] = k \overline{M}_v^{\,a}$$

Where k and a are const

Taking logs we get

$$\log [\eta] = \log k + a \log \overline{M}_v$$

The value of k and a depends on the nature of polymer, nature of the solvent and temp.

Knowing the value of a and k from plot of log $[\eta]$ vs $\overline{M}_v$ The value of $\overline{M}_v$ can be determined.

The value of $[\eta]$ is determined from the intercept of the graph of η_{red} vs c
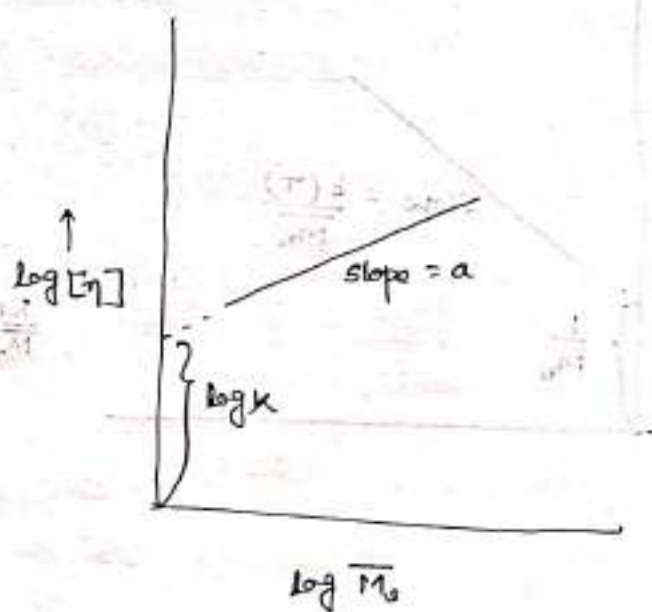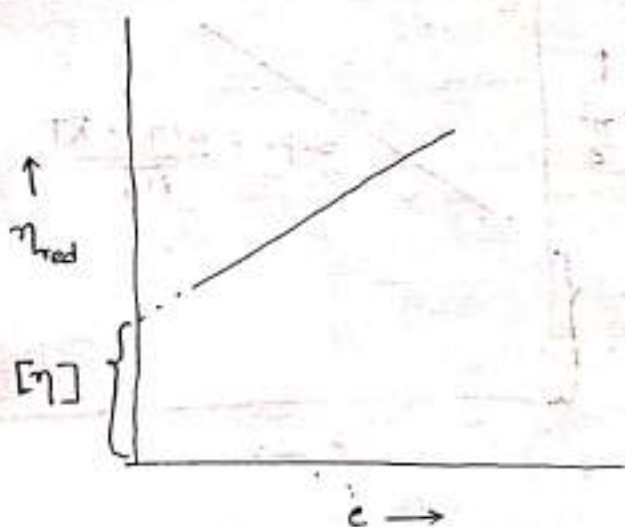
$$\eta_{red} = \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{1}{c}\left(\frac{\eta}{\eta_0} - 1\right)$$

$$\eta = \eta_0 + Bc + c'c + \cdots$$

The avg. molar mass obtained from viscometry is the $\bar{M}_v$. This follows from the following analysis

Since $[\eta]$ is a limiting value as $c \to 0$, the conc. effect it contains can be written as

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c}$$

For a polydisperse system, we get

$$\eta_{sp} = \sum_i \eta_{sp_i}$$

$$= \sum_i c_i [\eta]_i = \sum_i c_i (k M_i^a) \qquad \left[\because [\eta] = k \bar{M}^a \right]$$

Again $\quad c = \sum_i c_i$

Hence $\quad [\eta] = \lim_{c \to 0} \dfrac{\sum_i c_i (k M_i^a)}{\sum_i c_i}$

$$\Rightarrow k \bar{M}^a = \frac{k \sum_i c_i M_i^a}{\left(\sum_i c_i \right)}$$

$$\Rightarrow \bar{M}^a = \frac{\sum_i c_i M_i^a}{\sum_i c_i}$$

$$= \frac{\sum_i N_i M_i^{(a+1)}}{\sum_i N_i M_i}$$

$$\Rightarrow \bar{M} = \left[\frac{\sum_i N_i M_i^{(a+1)}}{\sum_i N_i M_i} \right]^{1/a}$$

For $a = 1$, $\bar{M}_v = \bar{M}_{m}$

For most polymer system, the value a lies in the range of 0.5 to 0.8

Light Scattering techniques

If a light beam is passed through a colloidal sol^n, it is possible to see the light beam from the sides. This is the well known Tyndal effect which results from the scattering of a part of beam of light by the colloidal particles in all direction.

In case of macromolecules, the colloidal particles are highly solvated and the gel particles consist of about 90 to 99% of solvent. The refractive index of such particles is not very different from that of the solvent.
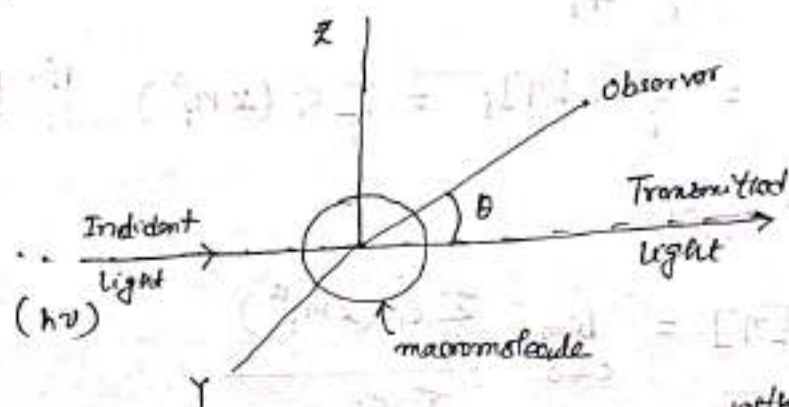
According to Debye eq^n turbidity (τ) of a system, is given as

$$\tau = \frac{32\pi^3}{3\lambda^4} \cdot \left(n\frac{dn}{dc}\right)^2 \cdot \frac{k_B T c}{\left(\frac{d\pi}{dc}\right)} \longrightarrow (1)$$

Where $\left(\frac{d\pi}{dc}\right)$ is the conc. dependence of eq^m osmotic pressure

λ = wavelength of the incident light

n = refractive index of medium

Now, we know osmotic pressure (π) is given as

$$\pi = RT\left[\frac{c}{M} + b(T)\left(\frac{c}{M}\right)^2 + \cdots\right]$$

$$\Rightarrow \frac{d\pi}{dc} = RT\left[\frac{1}{M} + 2 \cdot b(T) \cdot \frac{c}{M^2} + \cdots\right]$$

$$= RT\left[\frac{1}{M} + 2Bc + \cdots\right] \quad \left[B = \frac{b(T)}{M^2}\right]$$

$$\Rightarrow \frac{d\pi}{dc} = RT\left(\frac{1}{M} + 2Bc\right) \quad \left[\text{neglecting higher terms}\right]$$

Putting $\left(\frac{d\pi}{dc}\right)$ in eq^n (1) we get

$$\tau = \frac{32\pi^3}{3\lambda^4}\left(n\frac{dn}{dc}\right)^2 \cdot \frac{k_B T c}{RT\left(\frac{1}{M} + 2Bc\right)}$$

$$\Rightarrow \quad \tau = \frac{32\pi^3}{3\lambda^4}\left(n\,\frac{dn}{dc}\right)^2 \cdot \frac{1}{N_A} \cdot \frac{c}{\frac{1}{M}+2Bc}$$

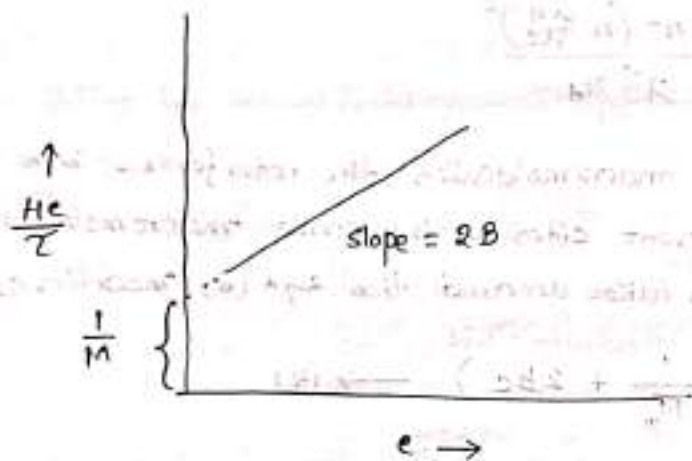$$\Rightarrow \quad \tau = \frac{Hc}{\frac{1}{M}+2Bc} \quad \longrightarrow (2)$$

where $\quad H = \dfrac{32\pi^3\left(n\,\frac{dn}{dc}\right)^2}{3\lambda^4 N_A} \quad$: Debye factor

Inverting eqⁿ (2) we got

$$\frac{1}{\tau} = \frac{\frac{1}{M}+2Bc}{Hc}$$

$$\Rightarrow \quad \frac{Hc}{\tau} = \frac{1}{M} + 2Bc \quad \longrightarrow (3)$$

Thus a plot of $\frac{Hc}{\tau}$ vs c is a straight line with intercept $\frac{1}{M}$

For polydisperse system, the molar mass is computed as below

$$c = \sum_i c_i \qquad \text{and} \quad \tau = \sum_i \tau_i$$

Thus $\quad M = \dfrac{\tau}{Hc} = \dfrac{\sum\limits_i \tau_i}{H\sum\limits_i c_i} \quad$ [when $c \to 0$ from plot]

$$\Rightarrow M = \frac{\sum\limits_i H c_i M_i}{H \sum\limits_i c_i} = \frac{\sum\limits_i c_i M_i}{\sum\limits_i c_i}$$

$$\Rightarrow M = \frac{\sum\limits_i N_i M_i^2}{\sum\limits_i N_i M_i} = \overline{M_m} \quad \longrightarrow (4)$$

Thus introducing polydispersy it is seen than M obtained in this plot is mass avg. molar mass $(\overline{M_m})$

Substitute eqn (4) in (5) we have

$$\frac{He}{\tau} = \frac{1}{M_m} + 2Bc \longrightarrow (5)$$

Now τ related to optical molar factor $R(\theta)$ or R_θ as

$$\tau = R_\theta = \frac{3\tau}{16\pi}$$

Hence eqn (5) becomes

$$\frac{He}{\frac{16\pi}{3} R_\theta} = \frac{1}{M_m} + 2Bc$$

$$\Rightarrow \frac{Kc}{R_\theta} = \frac{1}{M_m} + 2Bc \longrightarrow (6)$$

Where K is known as scattering cont i.e.

$$K = \frac{3H}{16\pi} = \frac{2\eta^2 \left(n \frac{d\eta}{dc}\right)^2}{\lambda^4 N_A}$$

For a sol^n containing macromolecules, the interference b/w the scattering light from different sites of the same macromolecules canna be excluded. If this is taken account, then eqn (6) modifies as

$$\frac{Kc}{R_\theta} = \frac{1}{P_\theta}\left(\frac{1}{M_m} + 2Bc\right) \longrightarrow (7)$$

Where $P_\theta = 1 + \frac{16\pi^2}{3\lambda^2} \overline{r_g^2} \sin^2 \frac{\theta}{2}$

where $\overline{r_g^2}$ = radii of gyration = $\frac{nl^2}{6}$

θ is the angle b/w scattered and transmitted Light

Hence now we can write

$$\frac{Kc}{R_\theta} = \left(1 + \frac{16\pi^2}{3\lambda^2} \overline{r_g^2} \sin^2 \frac{\theta}{2}\right)\left(\frac{1}{M_m} + 2Bc\right) \longrightarrow (8)$$

$$= \frac{1}{M_m} + S \cdot \sin^2 \frac{\theta}{2} + 2Bc + \cdots$$

Where $S = \frac{16\pi^2}{3\lambda^2} \overline{r_g^2} \cdot \frac{1}{M_m}$

From the eq^n (8), it is apparent that $\frac{Kc}{R_\theta}$ is linearly depend on conc. c (for a const. angle) and also on $\sin^2 \frac{\theta}{2}$ (provided c is held const.).

Zimm plot is the representation of light-scattering data which can be used to conduct the following extrapolation on a single graph

i) In limit, $c \to 0$ and $\theta = 0$, $\left(\frac{Kc}{R_\theta}\right)_{c=0, \theta=0} = \frac{1}{M_m}$

ii) In limit $\theta = 0$, $\left(\frac{Kc}{R_\theta}\right)_{\theta=0} = \frac{1}{M_m} + 2Bc$

iii) In limit $c = 0$, $\left(\frac{Kc}{R_\theta}\right)_{c=0} = \frac{1}{M_m} + S \cdot \sin^2 \frac{\theta}{2}$

End group analysis

The number avg. molecular weight ($\overline{M}_n$) of linear polymers can be determined by estimating the no of end groups by chemical analysis. For the successful application of the end group method, the number and nature of end groups per polymer molecule should be reliably known. This method is applicable to linear condensation polymer and also to add^n polymers. For example carboxyl terminated polybutadiene, hydroxyl terminated polybutadiene ; for detecting and analyzing qualitatively functional end-group of linear polymer, the amino end groups of nylon dissolves in m-cresol are readily determined by titrimetric method. From the knowledge of functional group equivalent and functionality, the molecular weight can be calculated using the following eq^n

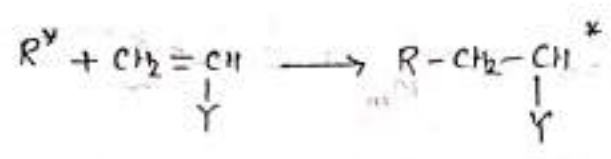$$\overline{M}_n = \frac{Functionality}{functional \ group \ eq^v.}$$

This method is limited to the determination of polymers with a molecular weight of less than 25,000.

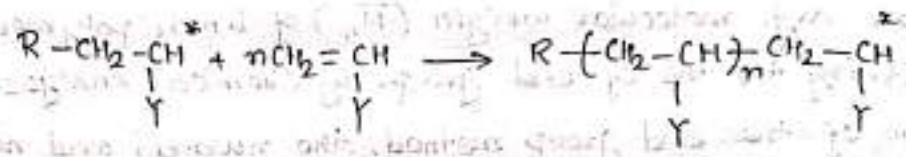# Kinetics of add^n polymerization

Add^n polymerization has the features of a chain reac^n. The reactive centre may be formed by reac^n with a free radical, a cation or an anion. Polymerization occurs through the propagation of the active species by the successive add^n of a large no. of monomer molecules in a chain reac^n occurring in a matter of a second or so at most, and usually in a much shorter time. By far the most common example of chain polymerization is that of the polymerization of vinyl monomers. The process can be as

Initiation

$$R^y + CH_2 = \underset{\underset{Y}{|}}{CH} \longrightarrow R - CH_2 - \underset{\underset{Y}{|}}{\overset{*}{CH}}$$

Propagation

$$R - CH_2 - \underset{\underset{Y}{|}}{\overset{*}{CH}} + nCH_2 = \underset{\underset{Y}{|}}{CH} \longrightarrow R - \left(CH_2 - \underset{\underset{Y}{|}}{CH} \right)_n CH_2 - \underset{\underset{Y}{|}}{CH}$$

The growth of the polymer chain ceases when the reac^n centre is destroyed by one of a no. of possible termination reac^n. The basic individual steps in the process are thus

i) Initiation (through UV ray / hv / γ-ray etc.)
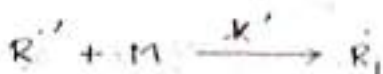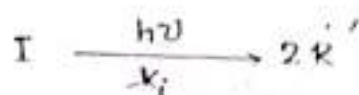ii) Propagation
iii) Termination

The driving force for the reac^n is provided by the relief in the steric strain by the change of sp^2 bonding to sp^3 bonding
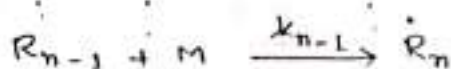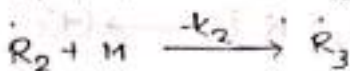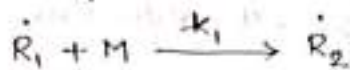
$$n\ CH_2 = \underset{\underset{Y}{|}}{CH} \longrightarrow \left(CH_2 - \underset{\underset{Y}{|}}{CH} \right)_n$$

sp^2

sp^3 bonding
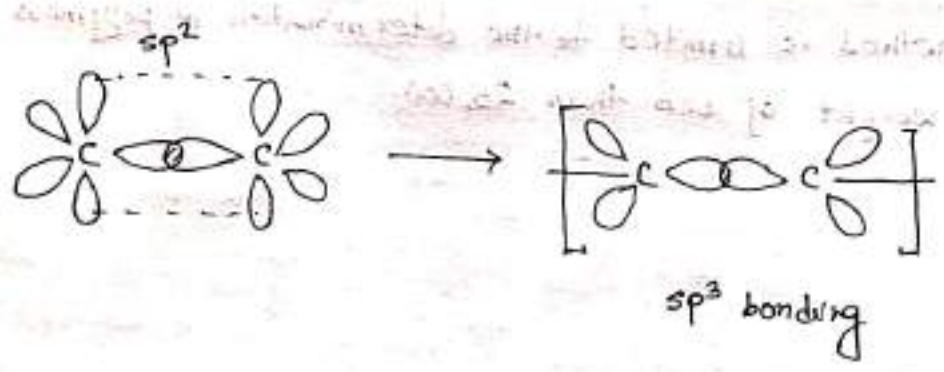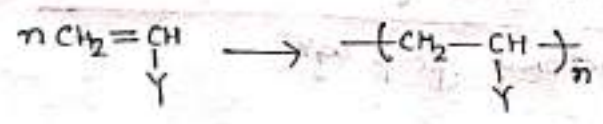
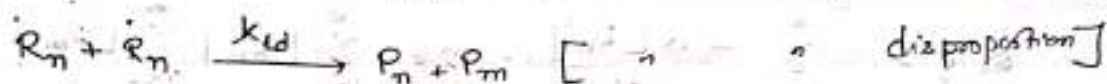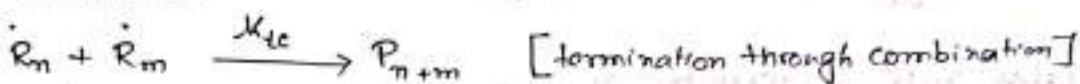# Mechanism and Kinetics of free radical add^n

i) Initiation

$$I \xrightarrow[\text{x_i}]{\text{$h\upsilon$}} 2\dot{R}'$$

$\begin{cases} I = \text{initiator} \\ R = \text{radical} \\ M = \text{monomer} \end{cases}$

$$\dot{R}' + M \xrightarrow{\text{k'}} \dot{R}_1$$

ii) Chain propagation

$$\dot{R}_1 + M \xrightarrow{k_1} \dot{R}_2$$

$$\dot{R}_2 + M \xrightarrow{k_2} \dot{R}_3$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$R_{n-1} + M \xrightarrow{k_{n-1}} \dot{R}_n$$

iii) Chain termination

$$\dot{R}_n + \dot{R}_m \xrightarrow{k_{tc}} P_{n+m} \qquad [\text{termination through combination}]$$

$$\dot{R}_n + \dot{R}_n \xrightarrow{k_{td}} P_n + P_m \qquad [\quad n \qquad , \qquad \text{disproportion}]$$

Now, rate of initiation will be

$$r_i = 2k_i[I] \longrightarrow (1)$$

$$r_i = \frac{d[\dot{R}_1]}{dt} = 2fk_i[I] = k'[\dot{R}'][M] \longrightarrow (2)$$

Assuming 'f' fraction of monomer is reacted at time t

Again total rate of propagation (r_p) will be

$$r_p = k_{1p}[\dot{R}_1][M] + k_{2p}[\dot{R}_2][M] + \cdots$$

Rate of propagation step does not depend on the chain length or size of the radical. so,

$$k_{1p} = k_{2p} = k_{3p} = \cdots = k_p$$

Putting this we get

$$r_p = k_p[M]\left\{[\dot{R}_1] + [\dot{R}_2] + [\dot{R}_3] + \cdots\right\}$$

$$\Rightarrow r_p = k_p[M]\sum_{n=1}^{\infty}[R_n] \longrightarrow (3)$$

Now, Rate of polymerization (r)

$$= \text{rate of consumption of monomer}$$

i.e. $$r = -\frac{d[M]}{dt}$$

Since consumption of monomer actually occurs in initiation and propagation

Thus, $r = r_i + r_p$

$$= k'[M][\dot{R}'] + r_p[M]\sum_{n=1}^{\infty}[\dot{R}_n] -$$

In the above equation propagation terms have infinity no. of terms. So, neglecting the r_i term and adding $n=0^{th}$ term, so that we get all the monomer unit without lost of any; it reduces as

$$r = k_p[M]\sum_{n=0}^{\infty}[\dot{R}_n] = k_p[M][\dot{R}] \longrightarrow (4)$$

From the termination steps

$$-\frac{d[\dot{R}_n]}{dt} = 2k_t[\dot{R}_n]\sum_{n=0}^{\infty}[\dot{R}_m] \quad ; \quad k_t = \frac{k_{tc} + k_{td}}{2}$$

Total rate of termination

$$\text{Bt } r_t = \sum_{n=0}^{\infty} -\frac{d[\dot{R}_n]}{dt} = 2k_t\sum_{n=0}^{\infty}[\dot{R}_n]\sum_{n=0}^{\infty}[\dot{R}_m]$$

$$= 2k_t[\dot{R}][\dot{R}] = 2k_t[\dot{R}]^2 \longrightarrow (5)$$

⊙ Introducing steady state approximation

$$\frac{d[\dot{R}']}{dt} = \frac{d[\dot{R}_i]}{dt} = \cdots = 0$$

i.e. $\frac{d}{dt}\left\{\sum_{n=0}^{\infty}([\dot{R}_n])\right\} = 0 \Rightarrow \frac{d[\dot{R}]}{dt} = 0$

For steady state approximation

$$r_i = r_t$$

$$\Rightarrow 2fk_i[I] = 2k_t[\dot{R}]^2$$

$$\Rightarrow [\dot{R}] = \left\{\frac{fk_i[I]}{k_t}\right\}^{1/2} \longrightarrow (6)$$

substituting equation (6) in (4) we got

$$r = k_p[M]\left\{\frac{fk_i[I]}{k_t}\right\}^{1/2}$$

$$= k_p\left(\frac{fk_i}{k_t}\right)^{1/2}[I]^{1/2}[M]$$

Factors affecting chain-polymerization

Ethylene, $CH_2=CH_2$ is the only aliphatic hydrocarbon which polymerizes well under free-radical mode of initiation. Propylene and isobutylene are unreactive under these condition. Electron density at the double bond may determine wheather a particular monomer polymerizes by anionic, cationic or free-radical mode.

Monomer str	Mode of initiation
$CH_2=C \overset{X}{\underset{\diagdown}{\diagup}}$	Cationic$^+$, eg. butene, styrene, vinyl ether
$CH_2=C \overset{X}{\underset{\diagdown}{\diagup}}$	Anionic$^-$, e.g. acrylonitrile, styrene
$CH_2=C \overset{X}{\underset{\diagdown}{\diagup}}$	free radical, ethyl acrylate

Initiators

A no. of polymerization are initiated by heat and UV radiation. Usually, the initiation is peroxide, hydroperoxide, an azo-nitrile, etc, which can readily be converted to free radical under the condition for the desired polymerization. One typical initiator is benzoyl peroxide

$$Ph-\overset{O}{\underset{\|}{C}}-O-O-\overset{O}{\underset{\|}{C}}-Ph \xrightarrow{h\nu} Ph-\overset{O}{\underset{\|}{C}}-\dot{O} \longrightarrow Ph + CO_2$$
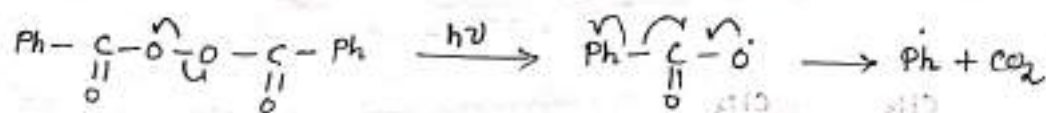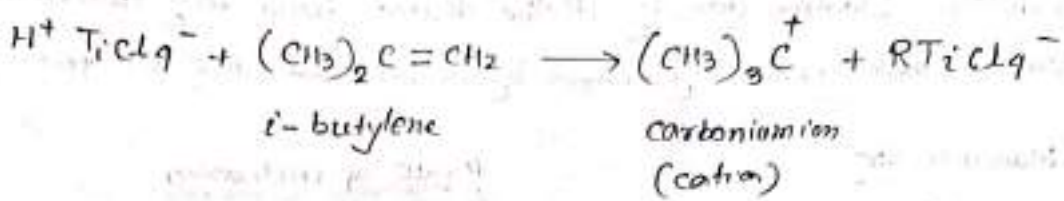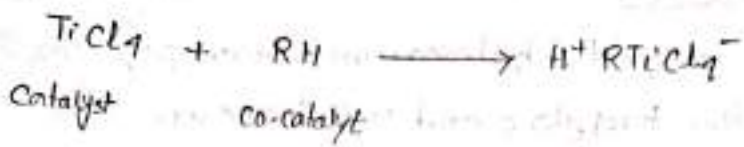
Ionic add^n polymerization

The polymerization of vinyl monomers can take place in the presence of a cation or an anion also.
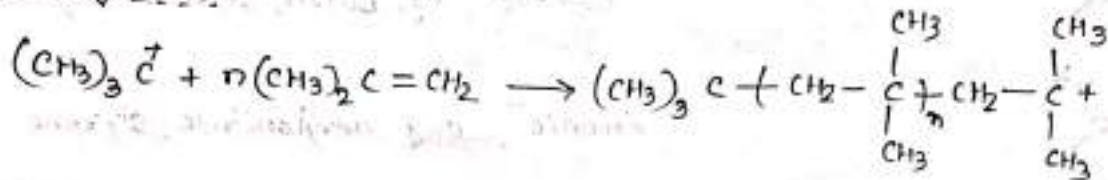
Cationic Polymerization

Cationic Polymerization differs from free-radical polymerization, specially in the initiation and termination steps. The initiator used are Lewis acid such as BF_3, $AlCl_3$, $TiCl_4$, H_2SO_4 and other strong protonic acid. All these, except possibly the strong protonic acids, need a co-catalyst to initiate the polymerization. The co-catalyst supplies hydrogen, and the real initiator is believed to be a proton in every case. This means that one end of the polymer is hydrogen atom. The monomers which best polymerize by cationic initiation are olefins substituted with electron releasing group (EDG) such as $CH_2=C(CH_3)_2$, $PhCH=CH_2$, etc.
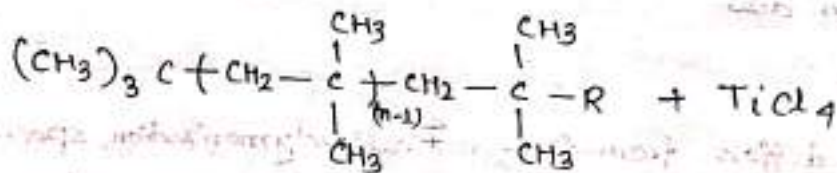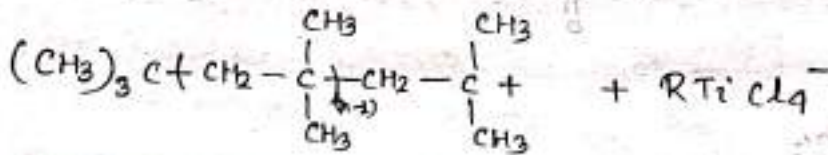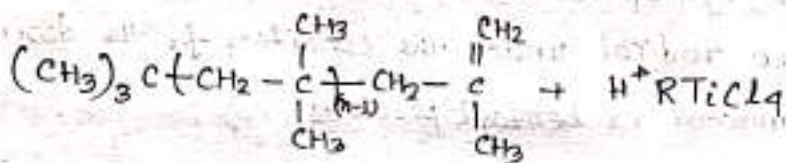
Initiation

$$TiCl_4 + RH \longrightarrow H^+ RTiCl_4^-$$

Catalyst   Co-catalyst

$$H^+ TiCl_4^- + (CH_3)_2 C = CH_2 \longrightarrow (CH_3)_3 \overset{+}{C} + RTiCl_4^-$$

i-butylene   Carbonium ion (cation)

Propagation

$$(CH_3)_3 \overset{+}{C} + n(CH_3)_2 C = CH_2 \longrightarrow (CH_3)_3 C + CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} \overset{}{\underset{n}{\Big]}} CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} +$$

Termination

$$(CH_3)_3 C + CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} \overset{}{\underset{(n-1)}{\Big]}} CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} + \quad + \quad RTiCl_4^-$$

$$\downarrow$$

$$(CH_3)_3 C + CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} \overset{}{\underset{(n-1)}{\Big]}} CH_2 - \overset{\overset{CH_2}{||}}{\underset{\underset{CH_3}{|}}{C}} \quad + \quad H^+ RTiCl_4$$

$$\downarrow$$

$$(CH_3)_3 C + CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} \overset{}{\underset{(n-1)}{\Big]}} CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} + \quad + \quad RTiCl_4^-$$

$$\downarrow$$

$$(CH_3)_3 C + CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} \overset{}{\underset{(n-1)}{\Big]}} CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - R \quad + \quad TiCl_4$$
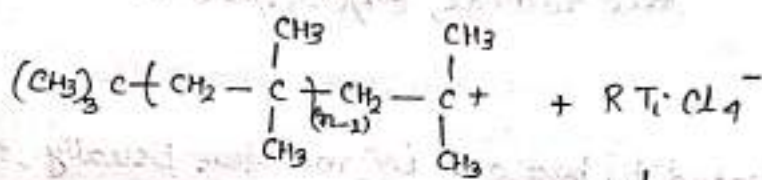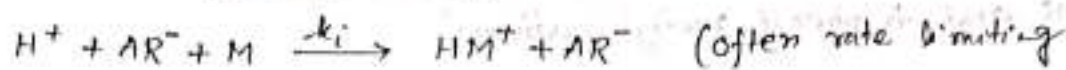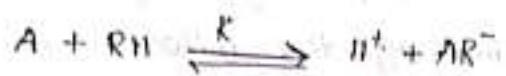
Polymerisation proceeds most rapidly to give the high molecular weight polymers at very low temp. For example i-butylene at -100°C gives a high polymer in a fraction of second. At room temp a dimer is formed slowly.
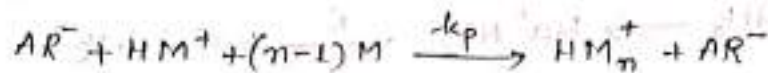
Kinetics of cationic polymerization

Most of the cationic polymerization proceed so rapidly that it is difficult to established the steady state. However, the following kinetic scheme seems to be valid, Let the catalyst be designated A and co-catalyst by RH. Then,
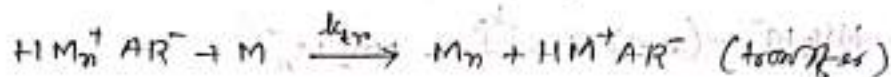
Initiation

$$A + RH \xrightleftharpoons{k} H^+ + AR^-$$

$$H^+ + AR^- + M \xrightarrow{k_i} HM^+ + AR^- \quad \text{(often rate limiting}$$

Propagation

$$AR^- + HM^+ + (n-1)M \xrightarrow{k_p} HM_n^+ + AR^-$$

Termination

$$HM_n^+ AR^- \xrightarrow{k_t} M_n + H^+ AR^-$$

$$HM_n^+ AR^- + M \xrightarrow{k_{tr}} M_n + HM^+ AR^- \quad \text{(transfer)}$$

Rate of initiation,

$$R_i = K k_i [A][RH][M]$$

If the formation of $H^+ AR^-$ is the rate determining step, R_t can be independent of $[M]$. The scheme is then appropriately modified. Since termination is first order,

$$R_t = k_t [HM^+ AR^-] = k_t [M^+]$$

Assuming steady state approximation

$$R_i = R_t$$

$$\Rightarrow K k_i [A][RH][M] = k_t [M^+]$$

$$\Rightarrow [M^+] = \frac{K k_i}{k_t} [A][RH][M]$$

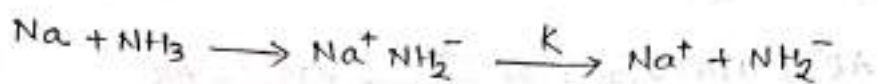Now overall rate of polymerization is decide by the propagation step

i.e. $$r = r_p = k_p [M][M^+]$$
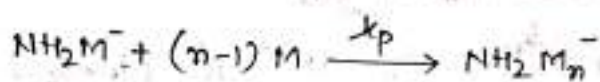
$$= K \cdot \frac{k_p k_i}{k_t} [A][RH][M]^2$$

Anionic polymerization

Monomers containing electron withdrawing group (EWG) or electronegative groups can polymerize by anionic mechanism. It was found that Na in Liq. NH_3 at $-75°C$ was a particularly effective initiator for the polymerization of α-methyl acrylonitrile, methyl acrylate, etc. were polymerized by this mechanism. Other effective initiator are Grignard reagent and triphenyl methyl sodium.
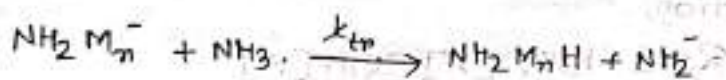
Initiation

$$Na + NH_3 \longrightarrow Na^+ NH_2^- \xrightarrow{k} Na^+ + NH_2^-$$

$$NH_2^- + M \xrightarrow{k_i} NH_2 M^-$$

Propagation

$$NH_2 M^- + (n-1) M \xrightarrow{k_p} NH_2 M_n^-$$

Termination

$$NH_2 M_n^- + NH_3 \xrightarrow{k_{tr}} NH_2 M_n H + NH_2^-$$
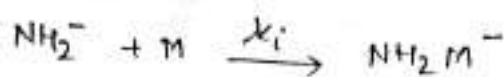
Rate of initiation, $r_i = k_i [NH_2^-][M]$

Applying steady state, $r_i = r_t$

$$\Rightarrow k_i [NH_2^-][M] = k_{tr} [NH_2 M_n^-][NH_3]$$

$$\Rightarrow [NH_2 M_n^-] = \frac{k_i}{k_{tr}} \frac{[NH_2^-]}{[NH_3]} [M]$$

Thus rate of polymerization

$$r_p = k_p [NH_2 M^-][M]$$

$$= \frac{k_i k_p}{k_{tr}} \frac{[NH_2^-]}{[NH_3]} [M][M]$$

$$= \frac{k_i k_p}{k_{tr}} \frac{[NH_2^-]}{[NH_3]} [M]^2$$

The above is the required rate expression.

The following example show the scope of this type.

initiation

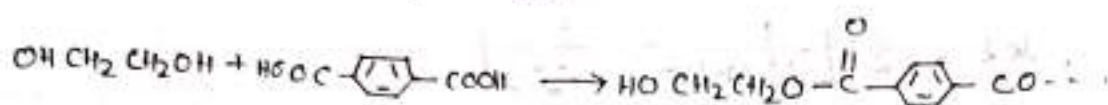$$RLi + CH_2 = \underset{\underset{Ph}{|}}{CH} \longrightarrow R - CH_2 - \underset{\underset{Ph}{|}}{CH} \; Li^+$$

Propagation
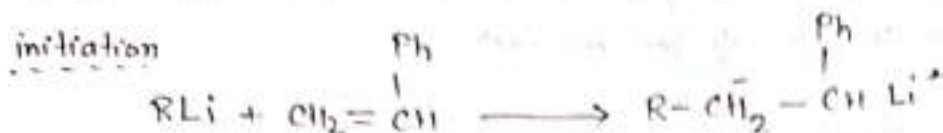
$$R - CH_2 - \underset{\underset{Ph}{|}}{CH} - Li^+ + (n-1)CH_2 = \underset{\underset{Ph}{|}}{CH} \xrightarrow{-H_2O} R - (CH_2 - \underset{\underset{Ph}{|}}{CH})_n$$
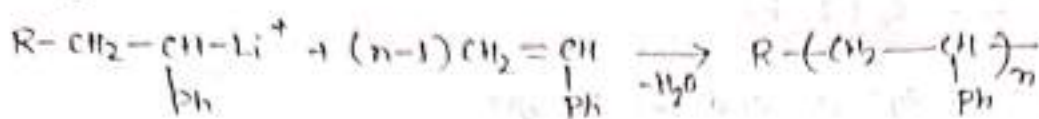
Kinetics of condensation (step growth) Polymerization

It may be discussed by the example of polyester formation b/w a dicarboxylic acid and ethylene glycol.

$$OH\;CH_2\;CH_2OH + HOOC - \langle\bigcirc\rangle - COOH \longrightarrow HO\;CH_2\;CH_2O - \overset{O}{\underset{||}{C}} - \langle\bigcirc\rangle - CO - \cdots$$

The above reac^n may proceed with or without the presence of an acid catalyst.

The acid catalysed rate of polymerisation may be written as

$$-\frac{d[COOH]}{dt} = k\,[COOH][OH][H^+]$$

$$= k'\,[COOH][OH] = k'\,[COOH]^2 \quad [k' = k\,[H^+]]$$

Because $[COOH] = [OH]$ because equimolecular amount of an acid and glycol are generally used. If c mol/lit be the conc. of acid and glycol then,

$$-\frac{dc}{dt} = k'c^2 \qquad \Rightarrow 2^{nd} \text{ order kinetics}$$

$$\Rightarrow \int \frac{dc}{c^2} = -k'\int dt \qquad \left\{ \begin{array}{l} \text{When } t = 0, \; c = c_0 \\ = \text{initial conc. of reactant} \end{array} \right.$$

$$\Rightarrow k't = \frac{1}{c} - \frac{1}{c_0} \longrightarrow (1)$$

If no external acid is used as catalyst i.e. for uncatalysed reac^n, one molecule of the dicarboxylic acid act as an catalyst. Then,

$$-\frac{d[COOH]}{dt} = k\,[COOH]^2[OH]$$

$$\Rightarrow -\frac{dc}{dt} = kc^3 \qquad \Rightarrow 3^{rd} \text{ order kinetics}$$

$$\Rightarrow \int \frac{dc}{c^3} = -k \int dt$$

$$\Rightarrow kt = \frac{1}{2}\left[\frac{1}{c^2} - \frac{1}{c_0^2}\right] \longrightarrow (2)$$

It is convinient to express the rate eq^n in terms of the extent of rxn P, rather than in terms of conc. of the reactant.

Again $\quad P = \dfrac{C_0 - c}{C_0} = \dfrac{N_0 - N}{N_0}$

$$\Rightarrow \quad c = C_0 (1-P)$$

Replacing this in eq^n (1) and (2) we get

$$k't = \dfrac{1}{C_0(1-P)} - \dfrac{1}{C_0}$$
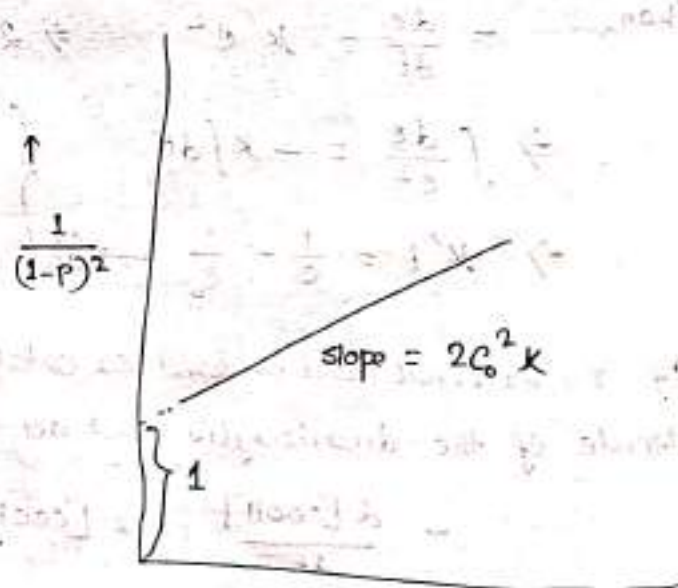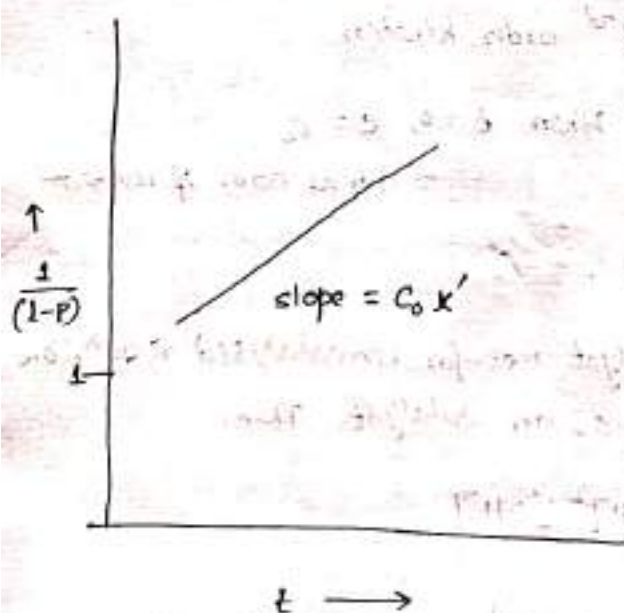
$$\Rightarrow \quad \dfrac{1}{1-P} = C_0 k' t + 1 \quad \longrightarrow (3)$$

and

$$kt = \dfrac{1}{2}\left[\dfrac{1}{C_0^2(1-P)^2} - \dfrac{1}{C_0^2}\right]$$

$$\Rightarrow \quad \dfrac{1}{(1-P)^2} = 2C_0^2 kt + 1 \quad \longrightarrow (4)$$

From eq^n (3) and (4) it is clear that for acid-catalysed polyesterification, a plot of $\dfrac{1}{(1-P)}$ vs t of polymerization should result a straight line.

Similarly for uncatalysed polyesterification a plot $\dfrac{1}{(1-P)^2}$ vs t should be linear.


From the slope we can calculate the value of rate const (K)

Co-ordination polymerization

There are a no. of coordination catalyst which can polymerize olefins. The most common catalyst of this type are composed of aluminium trialkyls and titanium or vanadium chloride. These catalyst are mostly effective for the polymerization of 1-olefins.
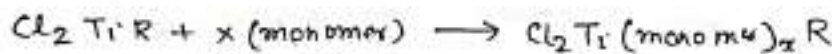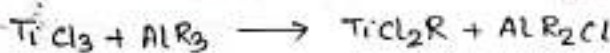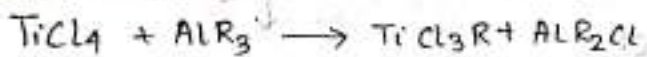
The Zeigler-Natta method, provide a heterogeneous-fibrous catalyst suitable for polymerization of olefines (ethylene).

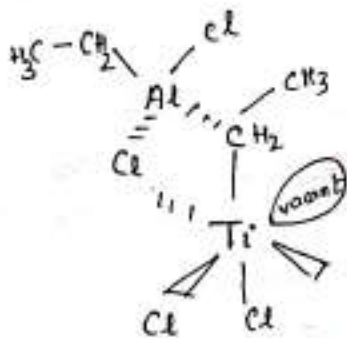$$n\ CH_2=CH_2 \xrightarrow[\text{catalyst}]{\text{Zeigler-Natta}} -(CH_2-CH_2)_n$$
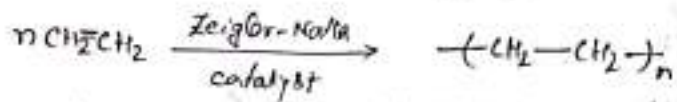
Zieglor discovered that combination of $TiCl_4$ and Al-E $AlEt_2Cl$ gave comparable activities for the production of poly ethylene. Natta used crystalline $\alpha-TiCl_3$ in combination with $AlEt_3$ to produce first isotactic polypropylene. i.e. two sets are

$$TiCl_3 \text{ and } AlCl_3$$
$$TiCl_4 \text{ and } AlEt_2Cl$$
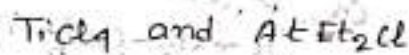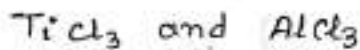
The following eqn seem to best describe the reason b/w titanium tetrachloride and a aluminium trialkyl.

$$TiCl_4 + AlR_3 \longrightarrow TiCl_3R + AlR_2Cl$$
$$TiCl_3R \rightleftharpoons TiCl_3 + \dot{R}$$
$$TiCl_3 + AlR_3 \longrightarrow TiCl_2R + AlR_2Cl$$
$$Cl_2TiR + x\ (monomer) \longrightarrow Cl_2Ti(monomu)_x R$$

Two type of str. have been put forward for the Zeiglar-Natta initiator a bimetallic (I) and monometallic (II) one.
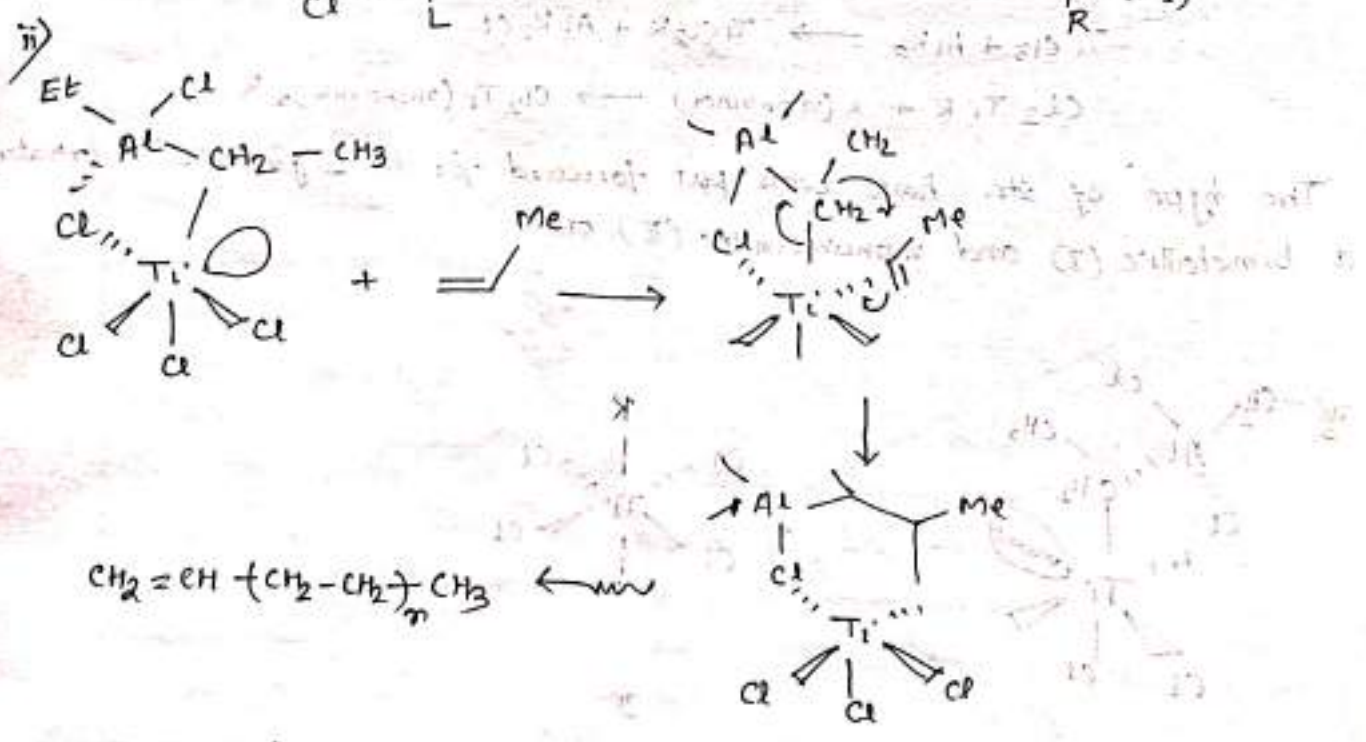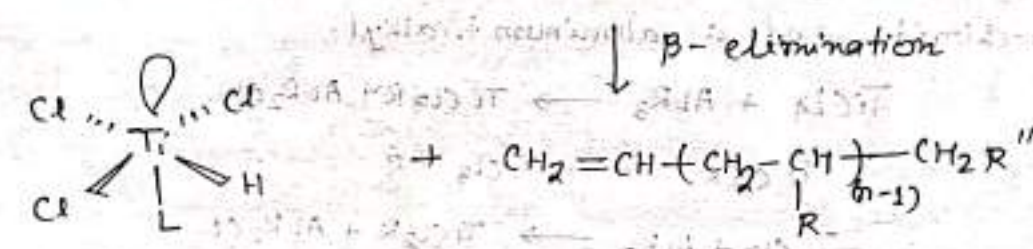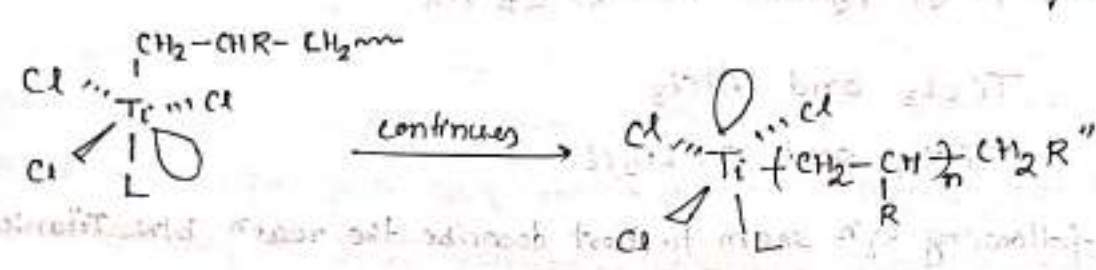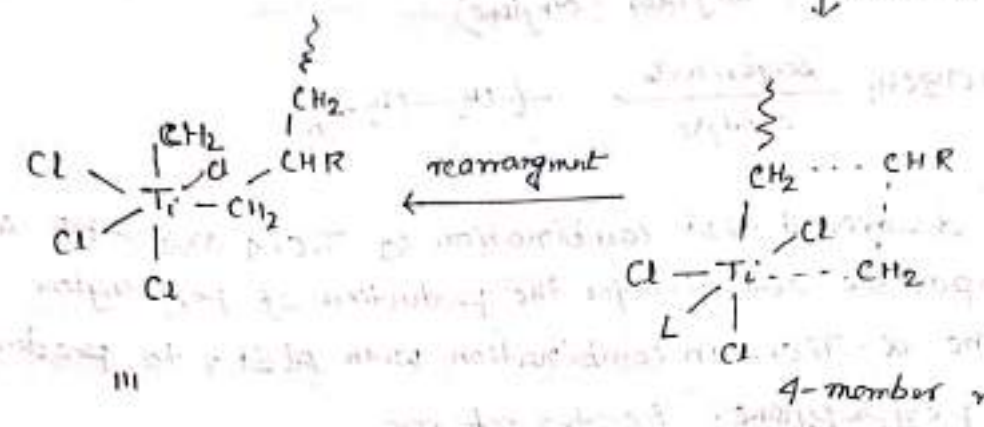

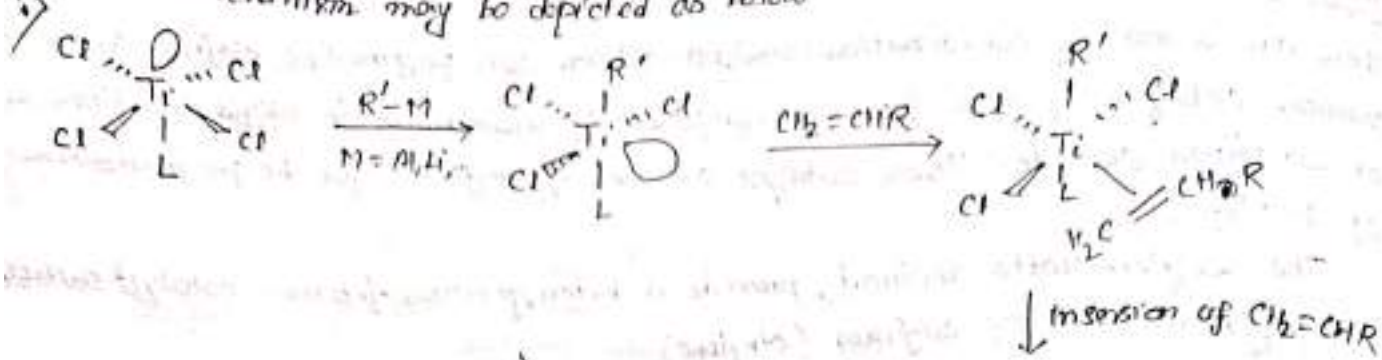I   II

L ≡ unspecified ligand

i) The mechanism may be depicted as below

$$Cl - Ti - O + \{CH_2 - CH\}_{\overline{n}} CH_2 R''$$

↓ β-elimination

$$+ \quad CH_2 = CH \{CH_2 - CH\}_{(n-1)} CH_2 R''$$
$$\qquad\qquad\qquad\qquad R_-$$

ii)

$$CH_2 = CH \{CH_2 - CH_2\}_{\overline{n}} CH_3 \longleftarrow$$

Co-polymerisation composition eqn

The composition of the co-polymer is most instances is found to be different from that of the co-monomer from which it is produced. In other words, different monomers have different de tendencies towards undergoing co-polymerization. Monomers M_1 and M_2 can each add either to propagating chain ending in M_1 or M_2.

$$\sim\!\!M_1^* + M_1 \xrightarrow{k_{11}} \sim\!\!M_1^*$$

$$\sim\!\!M_1^* + M_2 \xrightarrow{k_{12}} \sim\!\!M_2^*$$

$$\sim\!\!M_2^* + M_2 \xrightarrow{k_{22}} \sim\!\!M_2^*$$

$$\sim\!\!M_2^* + M_1 \xrightarrow{k_{21}} \sim\!\!M_1^*$$
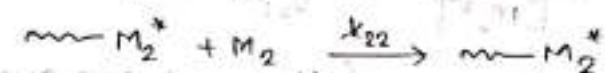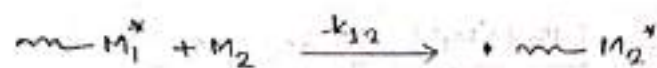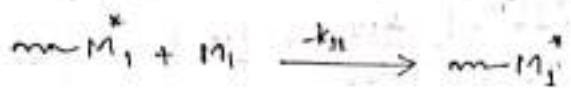
Where k_{11} is the rate const. for the addⁿ of an M_1^* radical to M, k_{12} is the rate cons. for the addⁿ of an m_i^* radical to M_2, k_{21} is the rate cont. for the addⁿ of an m_2^* of m_1, and k_{22} is the rate cons. for the addⁿ of an M_2^* to M_2.

The rate of disappearence of monomer M_1 and M_2 (neglecting any loss in the initiation process is given by

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \longrightarrow (1)$$

and

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \longrightarrow (2)$$

Dividing eqn (1) by (2) we get

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]}$$

$$= \frac{[M_1]}{[M_2]} \cdot \frac{k_{11}[M_1^*] + k_{21}[M_2^*]}{k_{12}[M_1^*] + k_{22}[M_2^*]} \longrightarrow (3)$$

Assuming steady state approximation, we get

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2]$$

$$\Rightarrow [M_2^*] = \frac{k_{12}}{k_{21}} \frac{[M_1^*][M_2]}{[M_1]} \longrightarrow (4)$$

Now reactivity ratio is given as

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}}$$

Multiplying both neumorator and donominartor by factor x of RHS of eq^n (s) we have

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{\frac{1}{k_{21}} \cdot \frac{[M_2]}{[M_2^*]} (k_{11}[m_1^*] + k_{21}[M_2^*])}{\frac{1}{k_{21}} \frac{[M_1]}{[M_2^*]} (k_{12}[m_1^*] + k_{22}[M_2^*])}$$

$$= \frac{[M_1]}{[M_2]} \cdot \frac{\frac{k_{11}}{k_{12}} \cdot \frac{[M_1^*][M_2]}{[M_2^*]} \cdot \frac{k_{12}}{k_{21}} + [M_2]}{\frac{k_{12}}{k_{21}} \cdot \frac{[M_1][M_1^*]}{[M_2^*]} + \frac{k_{22}}{k_{21}}[M_2]} \qquad \left\{ x = \frac{1}{k_{21}} \frac{[M_2]}{[M_2^*]} \right.$$

$$= \frac{[M_1]}{[M_2]} \cdot \frac{[M_1]r_1 + [M_2]}{[M_1] + r[M_2]} \qquad \left\{ \begin{array}{l} \text{Using worng } q \text{ and subatu} \\ r_1 \text{ and } r_2 \text{ value replace} \end{array} \right.$$

$$\Rightarrow \frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \longrightarrow (5)$$

Eq^n (5) is called co-polymer composition eq^n.

Various polymerization techniques

For laboratory and industrial purposs, polymerization is practised by a variety of approches and techniques that require different design consideration w.r.t. recipe of polymerization and, w.r.t. physical conditions for the proces and proces equipment. Generally, polymerizations are studied and practised by four different techniquse:

i) Bulk or mass polymerization

ii) sol^n Polymerization

iii) suspension polymerization

iv) Emulsion polymerization

Among all these four techniques, the last two are essentially heterogeneous polymerization system containing a large portion of a non-solvent, usually water acting as a dispersion medium for the immiscible liquid mononer. Both and sol^n polymerization may be either homogeneous all the way or heterogeneous, to begin with, but becoming heterogeneous with progres of polymerization due to the solvent used to dilute the monomer (for sol^n polymerization) or polymer formed being insoluble in it's monomer (for bulk polymerization). Most condensation polymerization are convinient done by employing bulk or the sol^n techniques.

Bulk polymerization

When a monomer is polymerized in bulk, an initiator which can decompose to give free-radicals at a fairly good rate at the temp of polymerization is used. There are advantages as well as disadvantages of this process. This method is now used for casting object to be preserved such as an insect, a flower or any other thing. This process can be carried out at comparitively low temp. Poly (methylmethacrylate) sheets and rods are made in this way. However, thermal control is difficult to achieve as also is any further isolation from the monomer.

Sol^n Polymerization

In sol^n polymerization, on the other hand, improved thermal control is possible, but it is difficult to remove the solvent. Further, chain-transfer to solvent may limit the molecular weight of polymer obtained. This limits the usefulness of the technique.

Emulsion and suspension polymerization

Emulsion and suspension polymerization is aqueous media are free from the problems of heat transfer, chain transfer and viscosity. These two methods have assumed industrial importance. It is possible to get higher molecular weights with emulsion polymerization. In emulsion polymerization, the monomer is emulsified in water with an emulsifying agent which may be a soap or detergent. Usually, a redox system is used. In a typical emulsion system a monomer(s), water, emulsifier (surfactant), a chain transfer agent and a water soluble initiator are usually used. ~~This is illustrated by the recipe~~