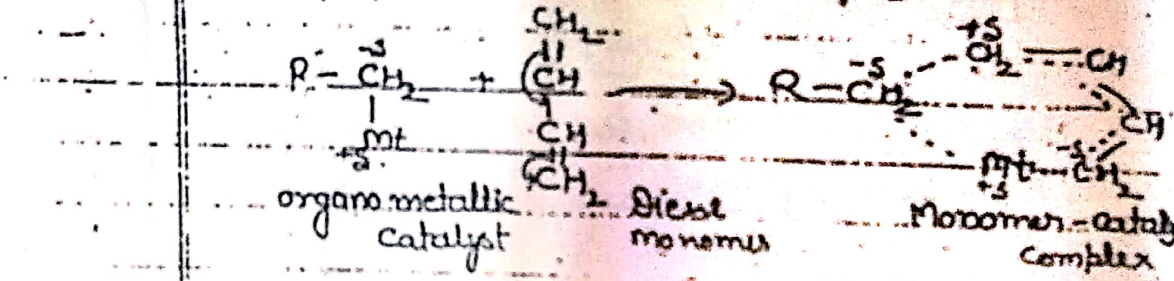
CO-ORDINATION POLYMERISATION

Polymerisation reactions of olefins & dienes taking place in presence of organo-metallic compounds as catalyst are called co-ordination polymerisation.

A co-ordination bond is formed b/w carbon atom of monomer and metal of catalyst.

Metals are transition metals like = Ti, Mo, V, Cr, Ni, Rh etc.

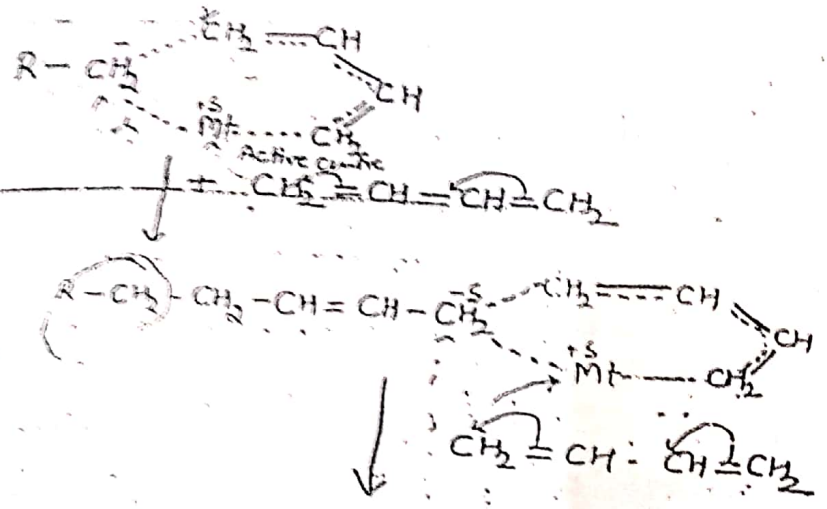
Initation step ⇒ (formation of complex b/w organometallic compound & monomer (catalyst)).

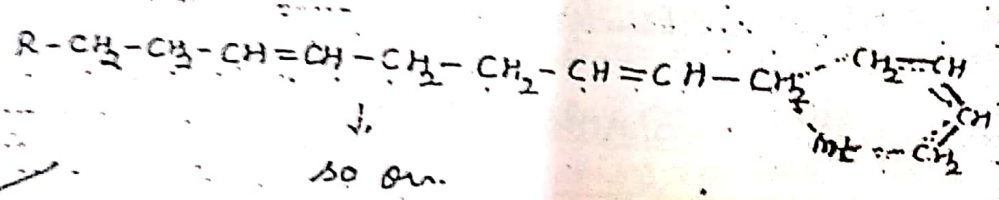


In the formation of the monomer-catalyst complex, a co-ordination bond is involved b/w a carbon atom of a monomer and metal of the catalyst, that is why the polymerisation is known as (co-ordination polymerisation.)

Propagation step ⇒ The co-ordinate metal-carbon bond formed in the monomer-catalyst complex acts as an active centre from where propagation step

The incoming monomer is incorporated at the active centre of the metal-C bond

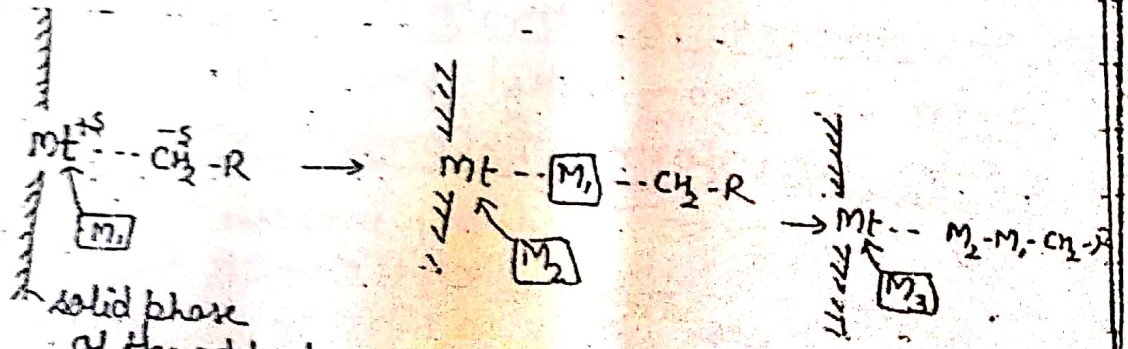


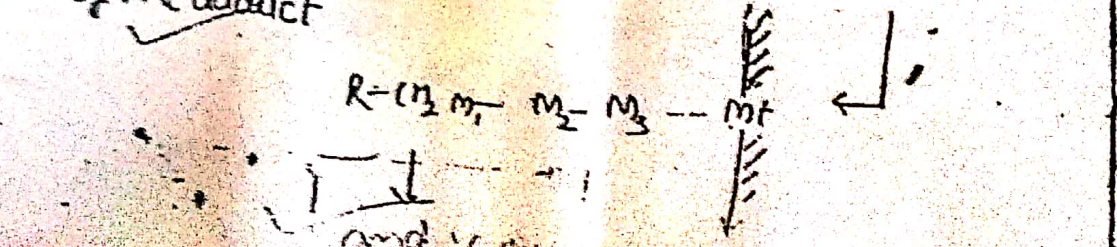


so on.

The monomer is inserted in b/w the metal ion and the carbanion with the result that the polymer chain formed is pushed out from the solid catalyst surface.

→ for this reason, co-ordination polymerisation is also known as insertion polymerisation





Ziegler-Natta catalyst ⇒

catalyst - halides of IV - VIII gp element

Co-catalyst - organo metallic compds
Generally Alkyls, aryls and hydride of gp I - IV^th

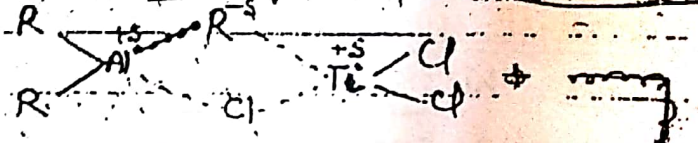
catalyst = Titanium chloride ($TiCl_3$ or $TiCl_4$)

Co-catalyst = $Al(C_2H_5)_3$ .. $Al(C_2H_5)_2Cl$.

* Aluminium alkyl act as a electron acceptor
Ti halide act as a electron donar

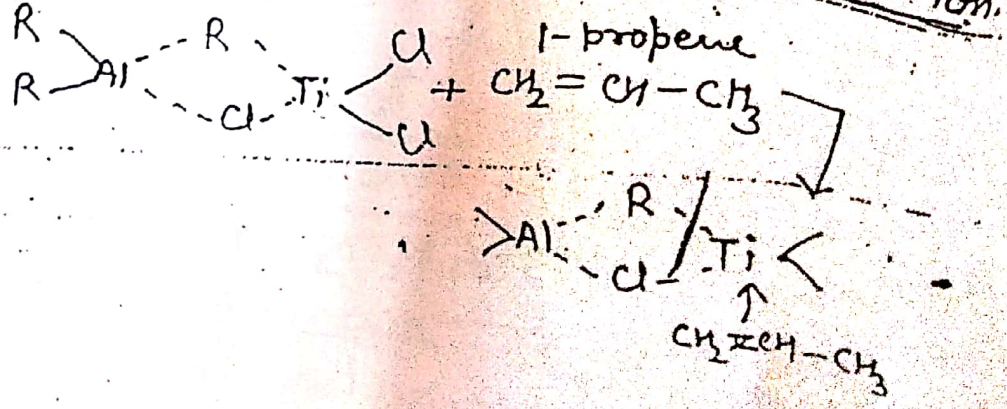
∴ Bimetallic mechanism ⇒ by Natta

① When catalyst & co-catalyst are mixed there is chemisorption of aluminium alkyl on $TiCl_3$ and form a bridge complex



This complex acts a active centre

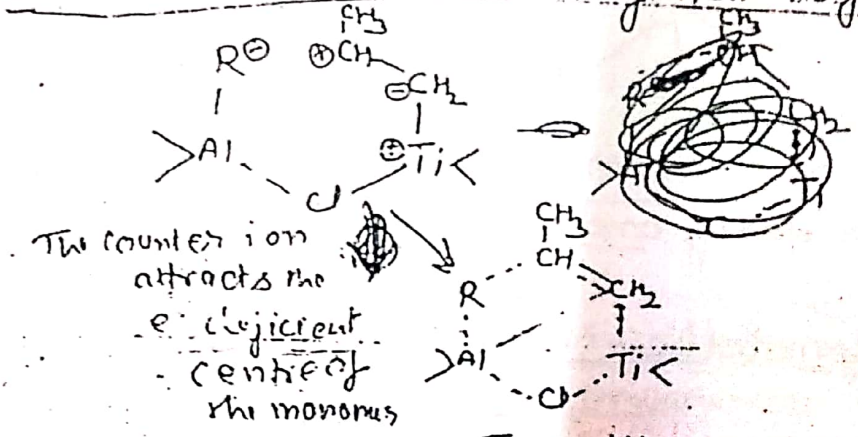
② The monomer is attract towards Ti–C bond (C from alkyl group R) in active centre and form π Complex with Ti ion.



(3) The bond b/w R and Ti breaks and form Ti ion [$Ti^{\oplus}$]

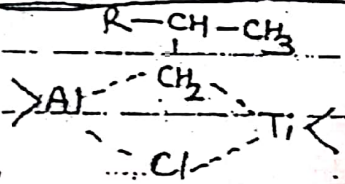
Ti ion forms bond

$Ti^{\oplus}$ ion attracts the πe's of monomer and thus transition state ring str. is formed

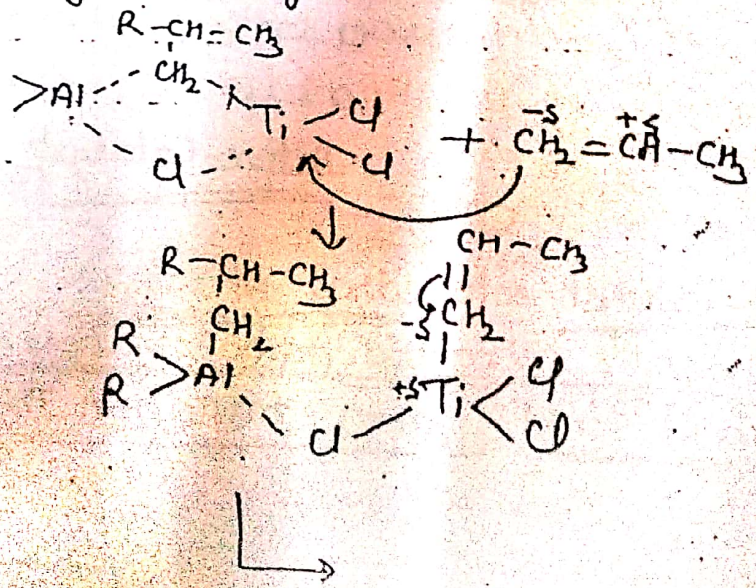


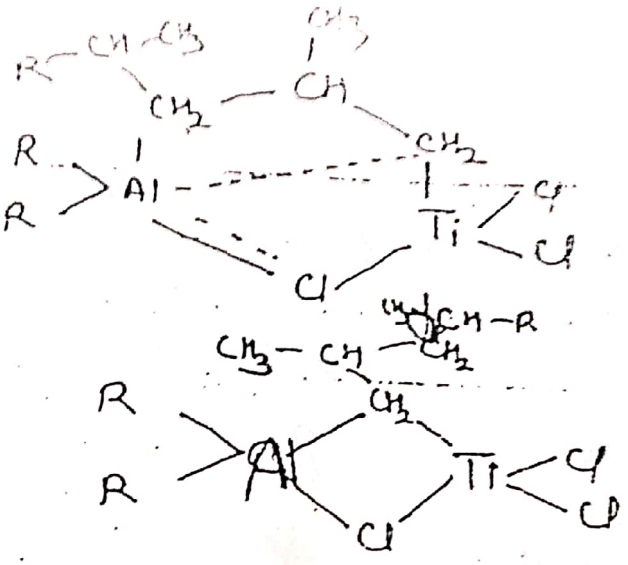
Transition state

(4) This transition state gives rise to the chain growth at metal carbon bond and form new active centre.



Thus the monomer is added repeatedly and polymer is formed.





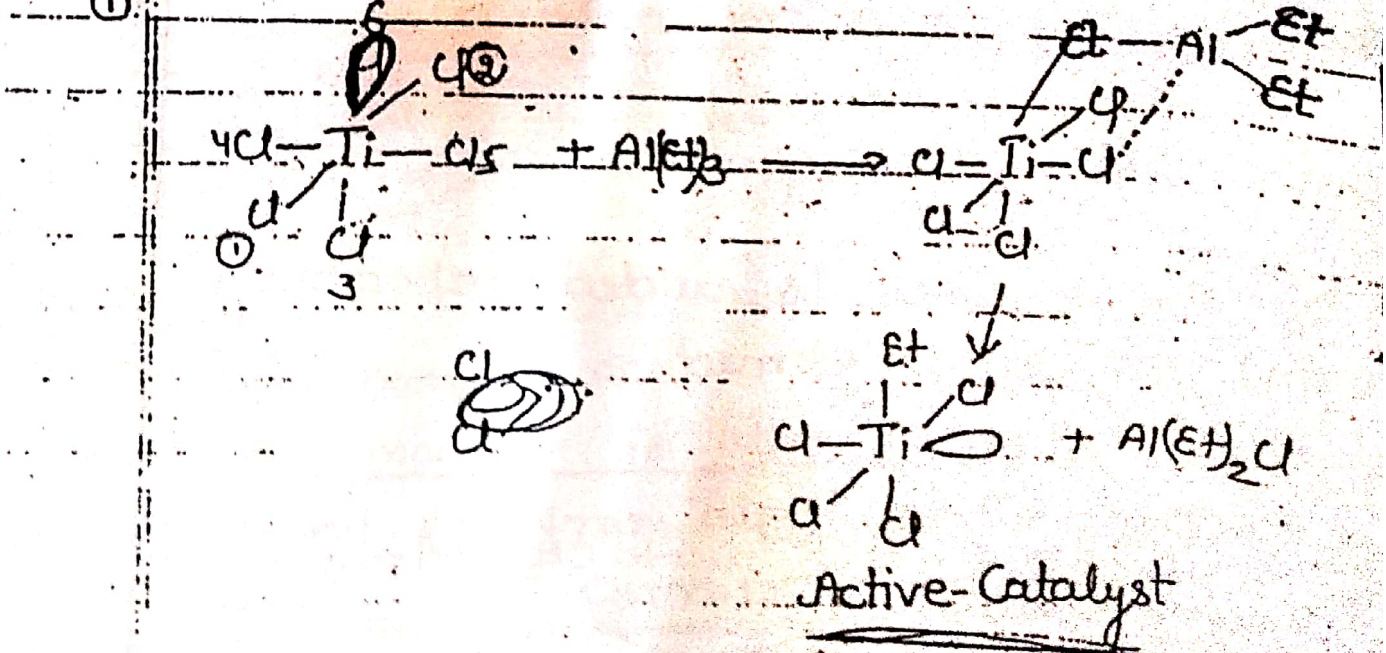
Thus the monomer is added ~~is added~~ repeatedly and polymer is formed.

Monometallic - Mechanism ⇒

given by cossee

→ Ti-R act as active centre

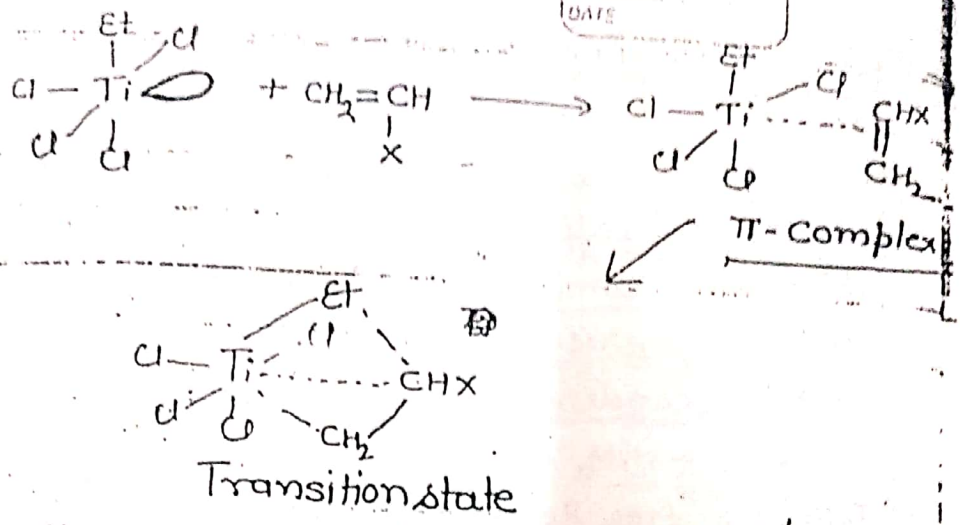
Used for the alkylation of the titanium chloride



Active-Catalyst

(i) Active-catalyst has octahedral structure.

Monomer is attracted towards the vacant d orbital and form transition π-Complex

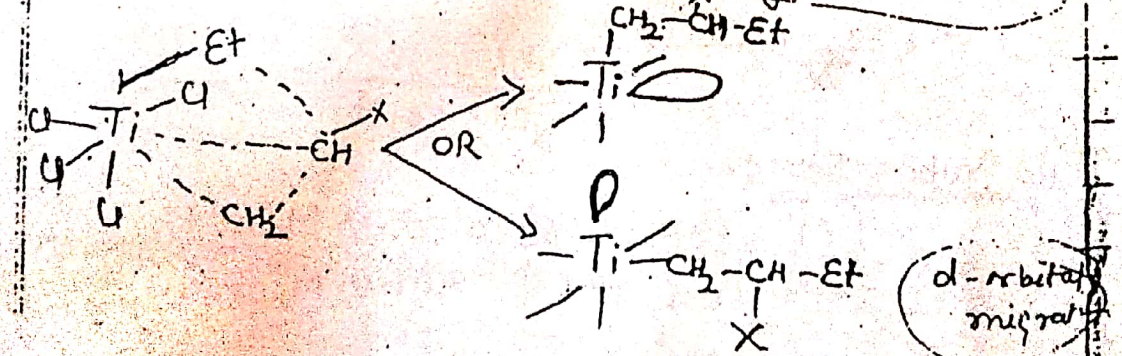


(i) This transition give rise to growth of polymer chain by the monomeric insertion at the Ti-Et bond.

(ii) Vacant d-orbital can be regenerated either at the same position or at the position of Ethyl.

(a) When vacant d-orbital is regenerated at same position all the time. Incoming monomer units will also have same position and isotactic polymer is formed.

(b) If d-orbital migrate from one position to another alternately, then polymers formed will be syndiotactic



STEREO-REGULAR POLYMERS

→ In stereo-regular polymers each monomer segment is in a regular configuration and this regular configuration gives structural regularity.

→ And this structural regularity arises by Geometrical and optical isomerism.

① optical isomerism ⇒ It means how different substituents are attached on asymetric carbon atom

ⓐ Isotactic polymers:- when R gps are present on one side of plane of c-c chain.

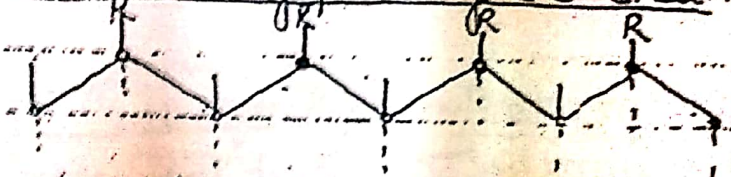


fig:- Isotactic

ⓑ Syndiotactic polymers :- when R groups are present alternately above & below the plane of carbon-carbon chain.

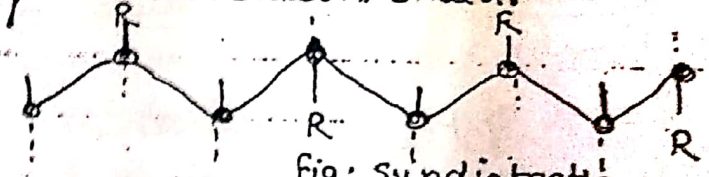


fig:- syndiotactic

ⓒ Atactic polymers ⇒ when R gps are present randomly.

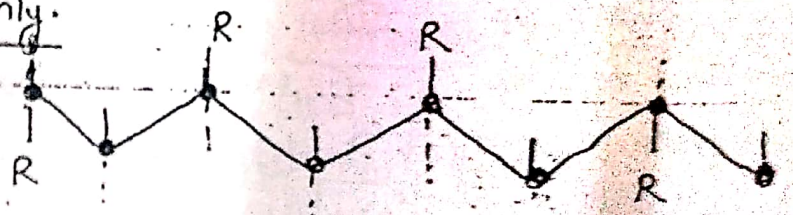


fig:- Atactic

→ These three types of polymers have different properties

① Isotactic and syndiotactic have high m.p & less soluble

② Atactic has low m.p & easily soluble

★ In optical isomerism ⇒ single bond (C-C) atoms are involved

Geometrical isomerism :-

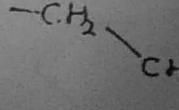
In this type of isomerism double bond C=C atoms are involved. It depends on how the different substituent are attached to carbon-carbon double bond.

Eg: 1,3 butadiene polymerisation.

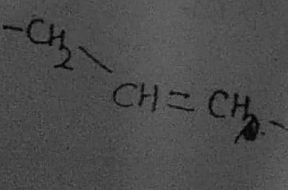
$$n\,CH_2=CH-CH=CH_2 \xrightarrow{\text{Polymerisation}} \{CH_2-CH=CH-CH_2\}_n$$

★ Isomerism depends on whether the CH_2 gps are close to or away from each other.

① Cis-configuration ⇒ when $-CH_2$ gps are on same side of double bond and close to each other (called cis-configuration)

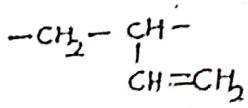


(ii) Trans-configuration ⇒ when $-CH_2$ gps are on opposite side and are not close.



(iii) 1, 2 vinyl configuration ⇒

In this case the three types of optical isomerism i.e atactic, isotactic and syndiotactic configuration are possible.



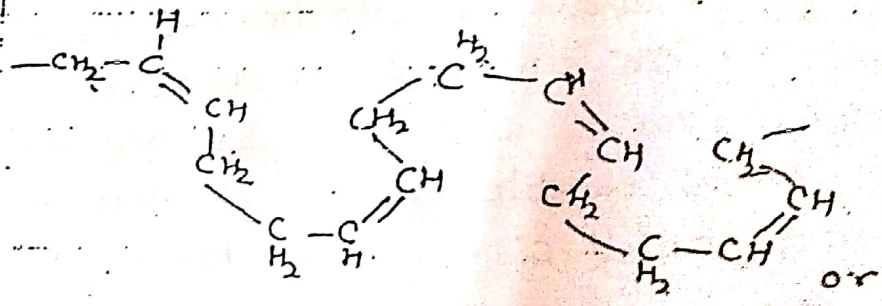
1, 2 vinyl configuration

★ In cis- configuration, there is a bending back of C-C chain.

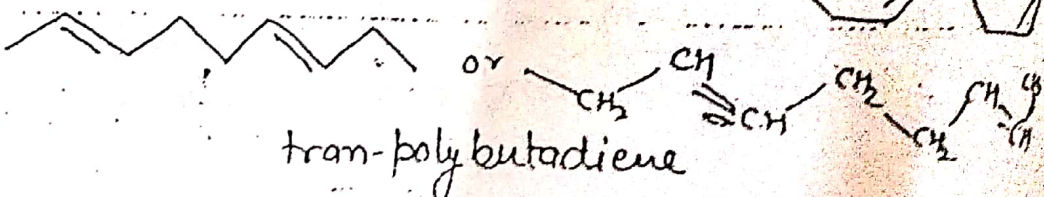
★ In trans- configuration there is a straightening out of the C-C chain.

∴ In 100% (cis- polymerisation of cis-butadiene molecules assumes shape of spring and has good elongation.

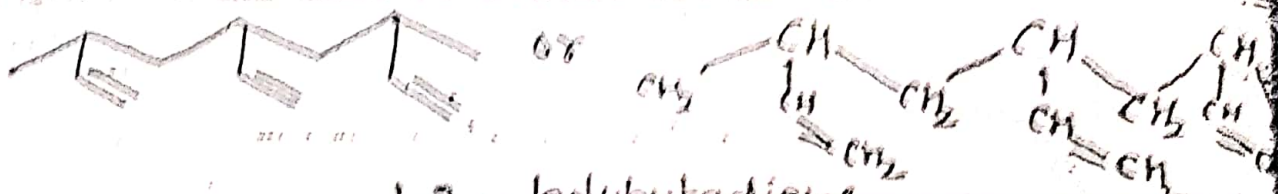
∴ In 100% trans-poly butadiene molecule has stiffness rod like structure and has less elongation.



cis-poly butadiene



tran-poly butadiene



1,2 - polybutadiene

fig : Configuration of 100% cis, 100% trans and 100% 1,2 polybutadiene molecules.

In practice, however, polymerisation of butadiene to 100% cis or 100% transis extremely difficult and we usually obtain mixtures of cis and Trans configuration.

Property of polymer depends on cis and Trans ratio.

U-II

Condensation / Step polymerisation

1. Poly condensation polymerisation
2. Poly addition polymerisation
3. Ring opening polymerisation

1. Poly condensation polymerisation ⇒

when the monomers contains active functional groups (generally two) which react together with the elimination of a simple molecule such as H_2O, NH_3 then the product formed is called condensation polymer and this phenomenon known as Poly condensation polymerisation

Exa: Nylon 66

which is formed by Hexamethylene diamine and adipic acid

$$NH_2-(CH_2)_6-NH_2 + COOH-(CH_2)_4-COOH \xrightarrow{-H_2O}$$

$$NH_2-(CH_2)_6-NH-CO-(CH_2)_4-COOH$$

formed product can react further either amine or acid because both side groups are free.

Then last product is Nylon 66

Kinetics of Polycondensation

In polycondensation reaction the reactivity of junction group is independent of the molecular size.

$$n\,A\text{-}A + n\,B\text{-}B \longrightarrow A\text{-}(AB)_{2n-1}\text{-}B + (2n-1)\,H_2O$$

To derive a mathmatical expression we take a exampie - The synthesis of polyester from a dicarboxylic acid & a diol.

① Self-catalysed esterification ⇒

This reaction is catalysed by mineral acids, but in the absence of mineral acid (such as H_2SO_4, HCl) the reactant carboxylic acid itself act as catalyst. for each step of reaction b/w Hydroxyl group & -COOH group.

$$-COOH + -OH \xrightarrow[\text{catalyst}]{+H^+} -COO^- + H_2O$$

⇒ The rate of the reaction can be measured by measuring the rate of disappearance of the Carboxylic group.

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

K = rate constant (considering equimolar, presence of - conc & ongles)

c - concentration of each group at a given point.

$-\frac{dc}{dt} = K\,[c]^2\,[c]$

$-\frac{dc}{dt} = Kc^3$

on integrating within the limits of c to c_0 (t to 0) we get

$-\int_{c_0}^{c} \frac{dc}{c^3} = \int_0^t K \cdot dt$ — ①

$\frac{1}{c^2} - \frac{1}{c_0^2} = 2Kt$

where c_0 = initial concn.

$2Kt = \frac{1}{c^2}$ – constant — ②

extent of fraction = P

i.e fraction of a given functional group that has reacted at time t then

$2Kt = \frac{1}{c^2}$ – constant

$\frac{c_0 - c}{c_0} = P$

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

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

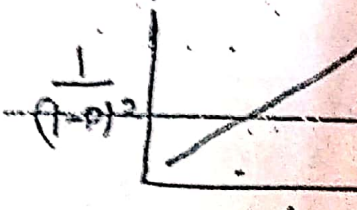
$$C = C_0(1-P) \quad \text{---} (3)$$

Combining eq (2) & (3)

$$2Kt = \frac{1}{[C_0^2 (1-P)^2]} \quad \text{— Constant} \quad \frac{1}{[C_0]^2}$$

$$\boxed{2C_0^2 Kt = \frac{1}{(1-P)^2} \quad \text{— Constant}} \quad (4)$$

This implies that a graphical plot of $\frac{1}{(1-P)^2}$ vs t must be linear.



for a simple esterification reaction, which proceeds without any side reaction, the number average of polymerisation may be related to P extent of polymerisation.

$$D_{Pn} = \frac{1}{1-P} = \frac{[C_0]}{[C]}$$

$$D_{Pn} = 2KC_0 t + 1$$

② Polyesterification using strong acids as catalyst

In this case the rate of disappearance of COOH groups can be then be expressed as

$$\frac{-d(COOH)}{dt} = k(COOH)(OH)$$

$$-\frac{dc}{dt} = kc^2$$

$C = C_0(1-p)$

$C_0 kt = \frac{1}{(1-p)}$

② Poly addition polymerisation ⇒

Poly addition polymerisation is brought about by the migration of atoms from one monomer unit to another or to the intermediate product.

for Exa: styrene can be polymerised in the presence of perchloric acid as follows.

$$CH_2=\underset{C_6H_5}{CH} + CH_2=\underset{C_6H_5}{CH} \longrightarrow C_6H_5\cdot CH-\underset{C_6H_5}{CH}=CH_2$$

$$\downarrow n\,CH_2=\underset{C_6H_5}{CH}$$

$$CH_3-\underset{C_6H_5}{CH}-\left(CH_2-\underset{C_6H_5}{CH}\right)_{n+1}-CH=\underset{C_6H_5}{CH}$$

simple addition at the double bond and and no free radical, carbanion. Carbonium is formed.

Monomer units are simply added one after another as in chain polymerisation to form a polymer such as H_2O, CO_2, HCl etc.

The polymer is formed by the migration of a hydrogen atom from a monomer and its addition at the double bond. This process involves a high activation energy required than the free radical polymerisation process.

Ring opening Polymerisation :-

* Monomer having a ring structure can be opened and polymerised if conditions are favourable. This 'opening up' is the opposite of the 'condensing process'.

* Some typical examples of ring opening polymerisation

Lactams, Lactones, cyclic ether, cyclic anhydride, Carboxy anhydride.

Ring opening polymerisation resemble chain polymerisation in the sense that it proceeds by addition of monomer units.

It also resemble step polymerisation in the sence that as polymer growth take place by step wise add of monomer unit.

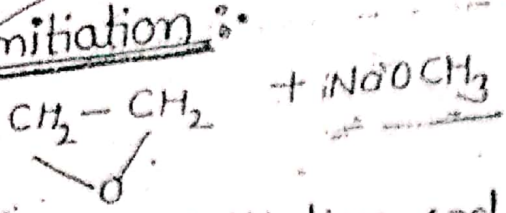
Cyclic ether :-

The polymerisation of eboxides such as ethylene and propylene oxide to high mol wt compounds can occur in many ways.

Lewis acid such as BF_3 give low mol wt polymer. so polymerisation of these epoxides are done by hydroxides, Alkoxides such as Sodium Methoxide ($NaOCH_3$).

The polymerisation occurs in three stages.

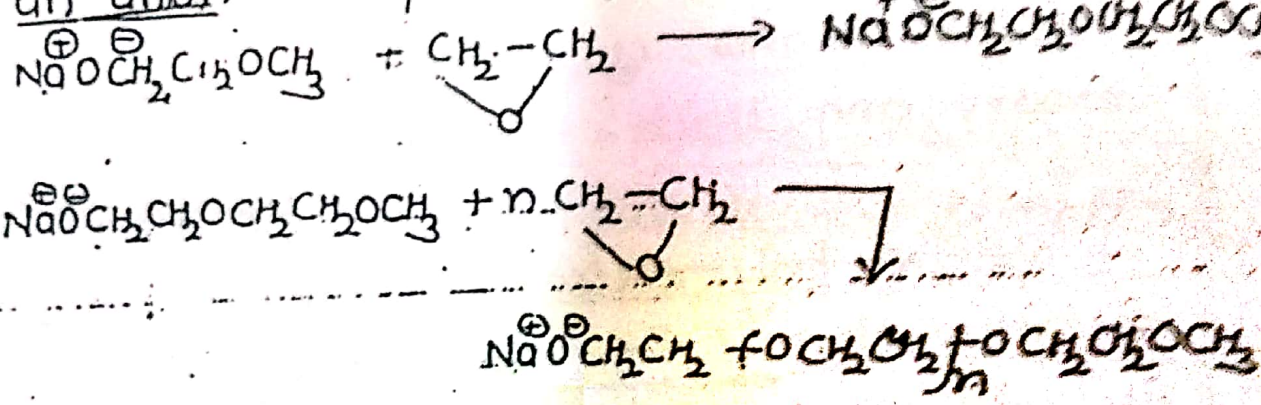
(i) Initiation :-



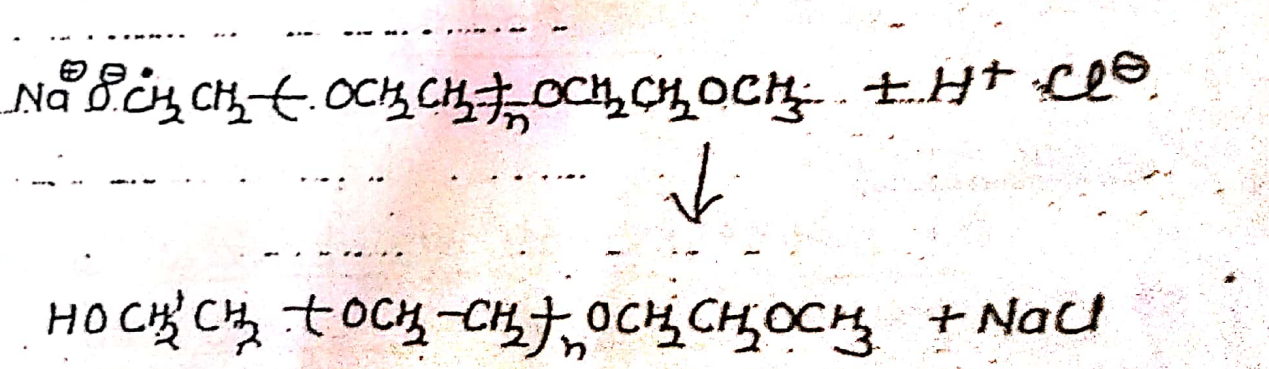
epoxide

In this initiation sodium methoxide attack the oxirane ring and cleave (break) the ring and form an anion.

(ii) Propagation :- The anion formed attack the ethylene oxide ring which will be opened and form an anion. This process goes on -



(iii) Termination :- It occur when anion is caged by adding a proton eg HCl.



But in case of unsymmetrical epoxide like propylene oxide it may occur that different polymers can form (depending upon the mode of opening of the ring)

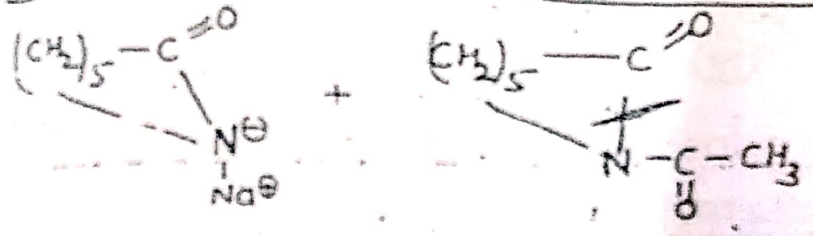
2008, 2006, 2010

Cyclic amide (Lactams) :-

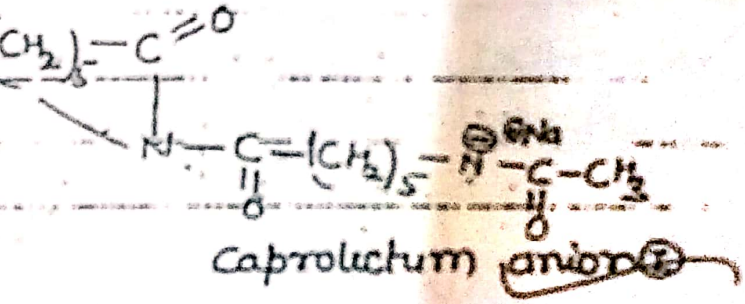
Ring opening polymerisation of Caprolactum form Nylon-6.

(i) Initiation :-

In this case sodium caprolactum and N-acetyl caprolactum (I) react and form the attacking anionic species called caprolactum anion (II)

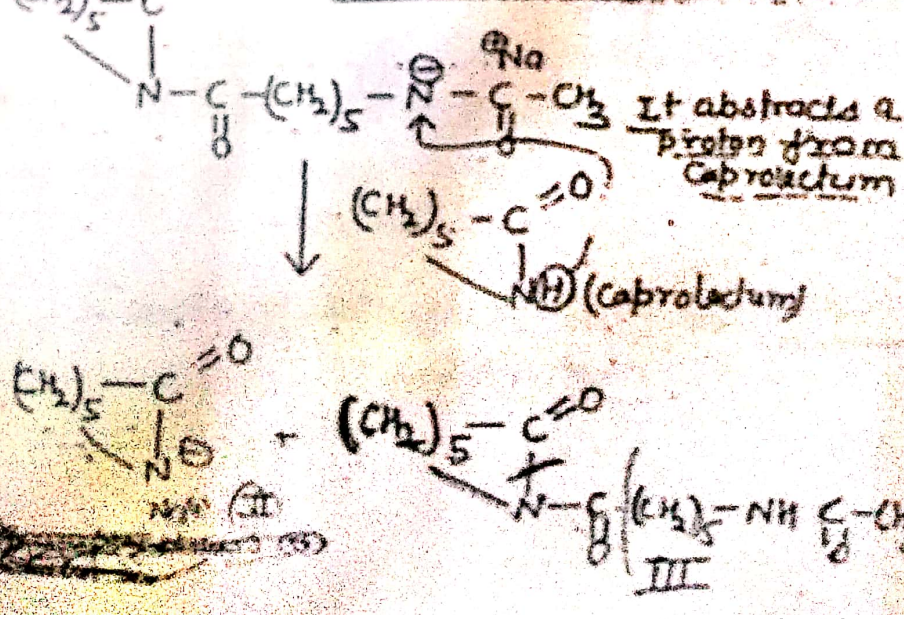


Sodium caprolactum N-acetyl caprolactum



Caprolactum anion (II)

(ii) Propagation :- caprolactum anion attack on another caprolactum molecule.



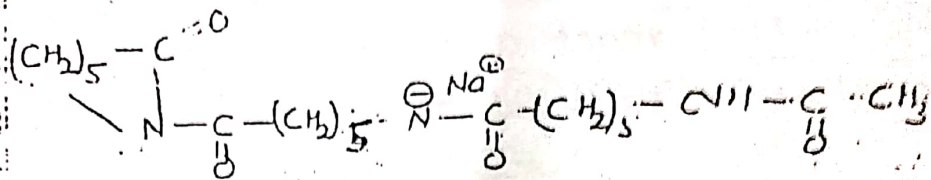
It abstracts a proton from caprolactum

(caprolactum)

III

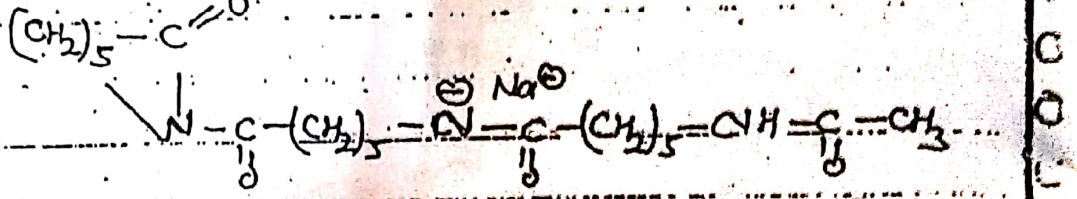
and forms a salt by the elimination of the monomeric anion].

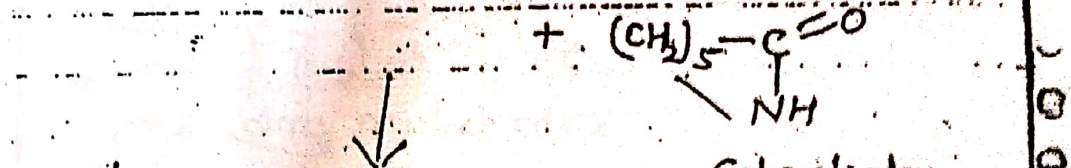
This new anion opens up the ring in the dimer (III) formed b/w the sodium caprolactum and N-acetyl caprolactum and gets it self attached, forming a trimer having again the anion (IV)



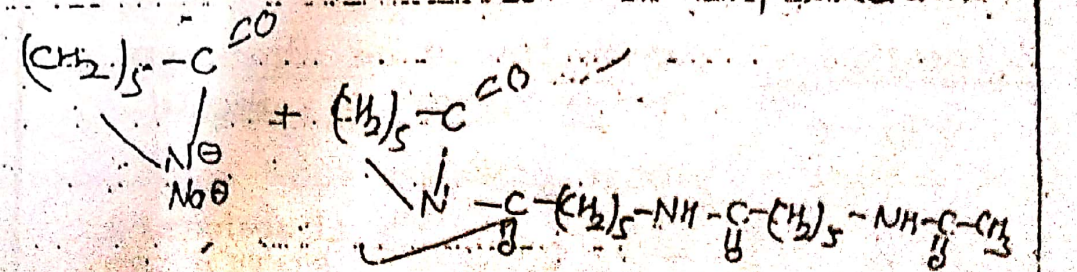
(IV)

This anion attack on caprolactum molecule and abstracts a proton and generating a new monomeric anion.





Caprolactum



and so on

(3) Termination = It occur by the proton abstraction.

Extent degree of Polymerisation :-

or stichiometric of reactant and degree of polymerisation

→ In polycondensation reaction two reactant are present in staichiometric equivalence

→ If there is a stoichiometric imbalance that is one of the reactant is present in the excess quantity. Then this imbalance

will show up on degree of polymerisation DP.

Consider a $RA_2 + RB_2$ polymerisation in which RB_2 is present in excess.

Reactant ratio r = (The ratio of the numbers of the different functional gps present initially.)

N_A = No. of reactive gp A-A

N_B = No. of reactive gp B-B

r = reactant ratio

$$r = \frac{N_A}{N_B} \quad -(6)$$

for linear step polymerisation

$N_A < N_B$ ... $r \leq 1$ ...

Now:

No. of reactive gps of A to start with $= 2N_A$

... B ... $= 2N_B$

So Total No. of reactive gp. $= 2N_A + 2N_B$ -(7)

from eq. (6) $N_B = \frac{N_A}{r}$

Putting this value in equation (7)

$$2N_A + 2N_A \quad \text{(cancelled)} \qquad 2N_A + \frac{2N_A}{r}$$

Total No. of reacting gp $= 2N_A + 2N_B = 2N_A\left(1 + \frac{1}{r}\right)$ -(8)

If: The fraction of gp B Consumed $= rp$

A $= p$

P is extent of reaction

we know that

$r \leq 1$ (equal or less than 1)

So,

the fraction of g.p. A remained unreacted $= 1-P$

and the fraction of g.p B remained unreacted $= 1-rP$

Total No of g.p remained unreacted =

$$\boxed{2N_A(1-P) + 2N_B(1-rP)} \quad -(9)$$

Now the degree of polymerization is given by

$$\bar{D}_p = \frac{[C_0]}{[C]} = \frac{2N_A\left(1+\frac{1}{r}\right)}{2N_A(1-P)+2N_B(1-rP)}$$

$$\boxed{\bar{D}_p = \frac{r+1}{r+1-2rP}}$$

* When no stoichiometric imbalance (i.e. both the reactants are present in stoichiometric equivalents)

$r=1$ and $\boxed{\bar{D}_p = \frac{1}{1-P}}$

When extent of conversion = 1 i.e. Polymerization goes to 100% completion $P=1$ then

$$\boxed{\bar{D}_p = \frac{1+r}{1-r}}$$

Unit III

CAROTHER'S-EQUATION

Carother developed a simple method of analysis for predicting the molar mass of polymers prepared by step polymerisation

If f = average functionality
P = Extent of reaction
$\bar{X}_n$ = average degree of polymerisation

Let N_0 be the total Number of reacting molecules initially present, giving an average functionality for the system as f

Let N be the Number of molecules present at time t when the extent of reaction is P

Then, number of molecules lost during the process over the time period t

$$t = (N_0 - N) ;$$

for each molecule lost, the number of functional groups lost is 2 (one of each kind) and hence the total number of functional gps lost is $2(N_0 - N)$ against the initial total number of $N_0 f$ functional gps.

$$\text{Extent of reaction } (P) = \frac{2(N_0 - N)}{N_0 f}$$

$$P = \frac{2}{f}\left(1 - \frac{N}{N_0}\right) \quad \text{—①}$$

$\frac{N_0 - N}{N_0}$

$\frac{N_0 + N}{N_0}$

The average degree of polymerisation = $\bar{X}_n$ or $\bar{DP}_n$

$$\bar{X}_n \text{ or } \bar{DP}_n = \frac{N_0}{N} \quad \text{---(2)}$$

$$= \frac{\text{Number of molecules present initially}}{\text{Number of molecules reacting at time } t}$$

Combining equation (1) & (2)

$$\boxed{P = \frac{2}{f}\left(1 - \frac{1}{\bar{DP}_n \text{ or } \bar{X}_n}\right)} \quad \text{---(3)}$$

This is carother equation.

for bifunctional groups $f = 2$.

$$P = \left(1 - \frac{1}{\bar{X}_n}\right)$$

$$\text{or } \boxed{\bar{X}_n = \frac{1}{1-P}} \quad \text{---(4)}$$

This equation is applicable to $RA_2 + RB_2$, RAB and M_2 polymerisation, in which there is an exact stoichiometry balance in the number of reactive functional gp.

If the mean molecular weight of the repeat unit in the polymer molecule is $= M_0$

Then average molecular weight

$$\boxed{\bar{M}_n = \bar{X}_n \cdot M_0 = \frac{M_0}{(1-P)}} \quad \text{---(5)}$$