

## 6

1- Chain Initiation :- Homolytic cleavage to form free radicals.

$$R-\overset{\text{O}}{\parallel}{C}-\underset{\text{peroxide}}{O}-\underset{\text{unstable}}{O}-\overset{\text{O}}{\parallel}{C}-R \xrightarrow{\Delta} 2 R-\overset{\text{O}}{\parallel}{C}-O^{\cdot} \longrightarrow 2 R^{\cdot} + 2 CO_2 \uparrow$$

f.r.

$$R^\bullet + \text{CH}_2=\text{CH} \xrightarrow{\text{F.R.}} R-\text{CH}_2-\dot{\text{C}}\text{H}$$

monomer 1.

to give new propagates -

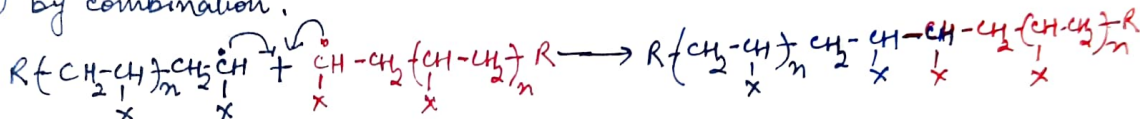
$$R-CH_2-\dot{C}H + \underset{\substack{| \\ \times \\ \text{monomer-2.}}}{CH_2=CH} \longrightarrow R-CH_2-\underset{\substack{| \\ \times \\ \text{New F.R.}}}{CH}-CH_2-\underset{\substack{| \\ \times}}{\dot{C}H}$$

$$\xrightarrow{CH_2=CH} R-CH_2-\underset{\substack{| \\ \times}}{CH}-CH_2-\underset{\substack{| \\ \times}}{CH}-CH_2-\underset{\substack{| \\ \times}}{\dot{C}H}$$

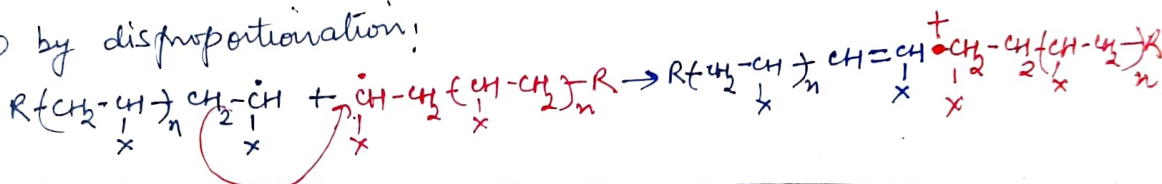
or

$$R(CH_2-\underset{\substack{| \\ \times}}{CH})_n-CH_2-\underset{\substack{| \\ \times}}{\dot{C}H}$$

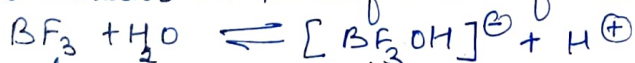
(a) by combination!



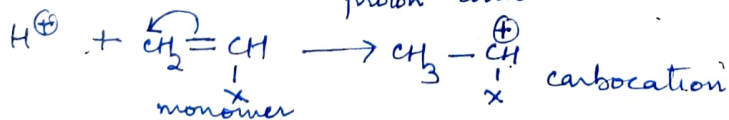
(b) by disproportionation:



1- chain initiation :-  $\text{H}_2\text{SO}_4, \text{BF}_3, \text{AlCl}_3, \text{SnCl}_4$  etc. are generally used as chain initiator in pres. of a trace of water.

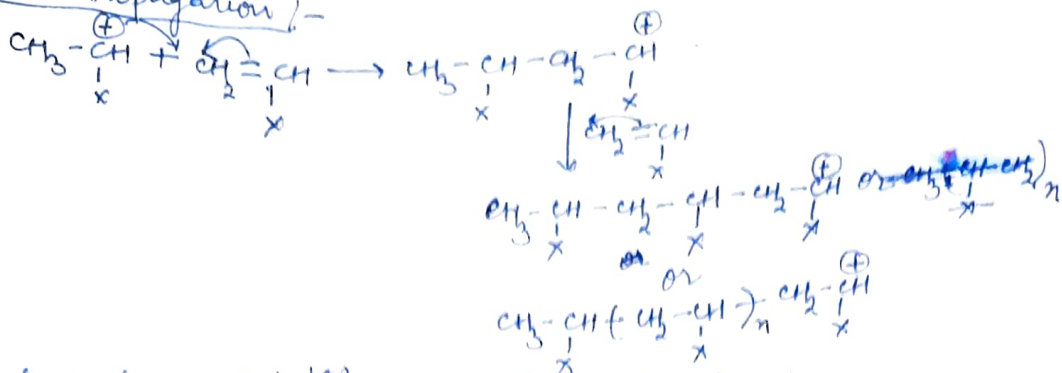


In general

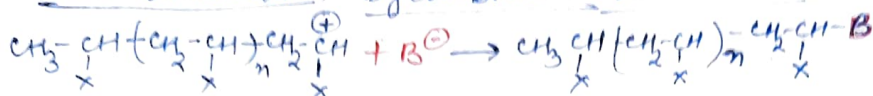


2- Chain propagation :-

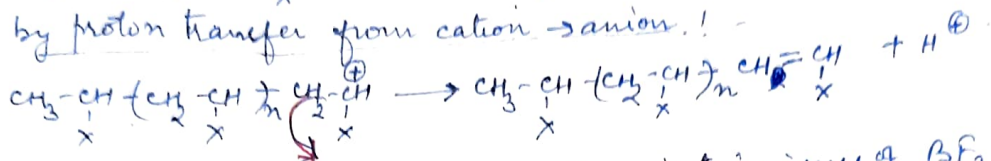
## 2-chain Propagation :-



## 3-chain termination :- (a) By combination with anion :-



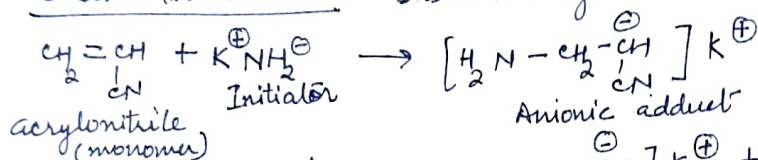
## (b) by proton transfer from cation to anion :-



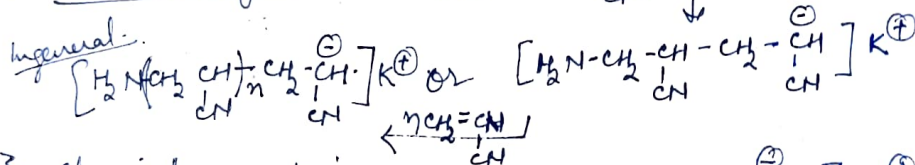
e.g. Isobutylene undergoes cationic polymerisation in the presence of  $\text{BF}_3$ .

## ANIONIC POLYMERISATION :-

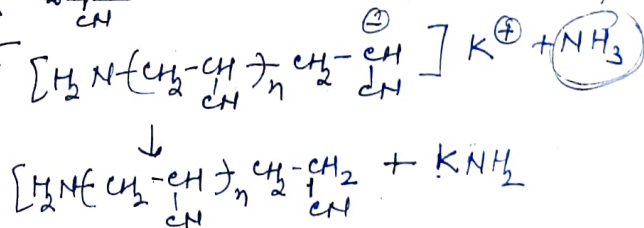
### 1-chain Initiation :- Bases or organometallic compds.



### 2-chain propagation :-



### 3-chain termination :-

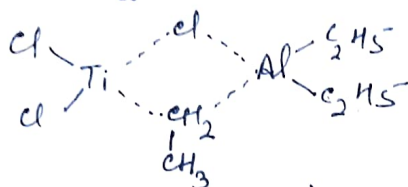
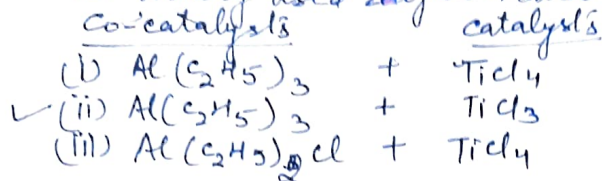


# Co-ordination polymerisation or Ziegler Natta Polymerisation

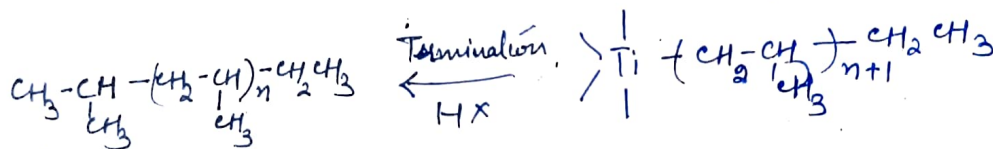
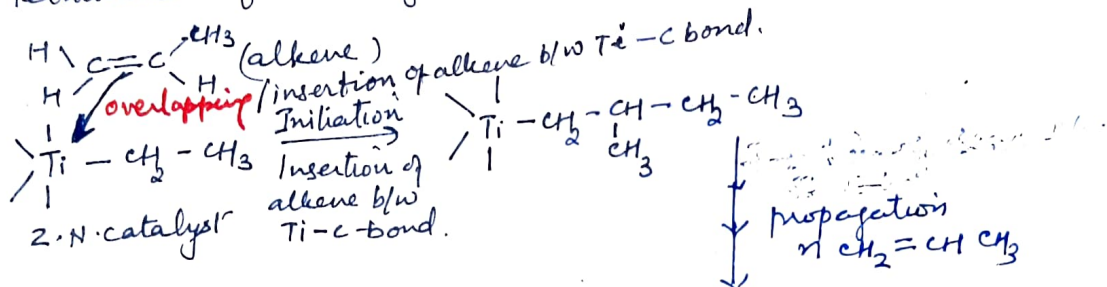
Coordination addition polymer is catalysed by a special type of Co-ordination catalyst known as Ziegler-Natta catalyst. It comprises of two components -

- (i) Halides of transition metals from gp IV - VIII (e.g. Ti, Fe, Mo, V, Ni, Rh etc) known as catalyst.
- (ii) Organometallic compounds e.g. hydrides, aryls or alkyls of gps I - IV metals are known as co-catalysts.

Most widely used Ziegler-Natta catalysts are: -



- Mechanism:
- (i) Formation of complex due to overlapping of  $\pi$  cloud of alkene and empty orbital of Ti.
  - (ii) Insertion of alkene b/w Ti & C in Ti-C bond.
  - (iii) Generation of vacant site at Ti due to intramolecular rearrangement and propagation of chain by step (i) & (ii).
  - (iv) Termination of chain by molecules having active H.



- Significance:
- (i) This polymer is stereoselective (gps are arranged in definite order) and hence permits Stereochemical control. Preferentially isotactic (highly stereoregular) polymers are formed by this method. Isotactic have superior priority than atactic.
  - (ii) It leads to the formation of linear chain polymers, devoid of branching having high density, high m.p., proper packing.