Atmospheric oxygen is a good inhibitor and it is because of its biradical nature.

$$P^{\cdot} + \dot{O}-\dot{O} \longrightarrow P-O-O^{\cdot} \xrightarrow{\cdot P} P-O-O-P$$

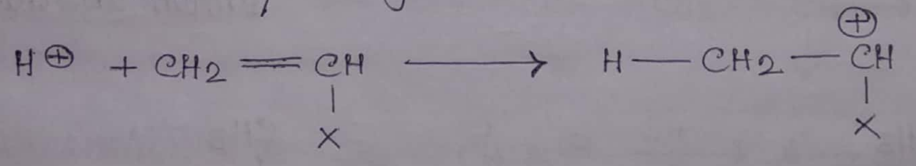
This is why, radical polymerisation is generally carried out a N_2 – atmosphere to aviod the atmospheric oxygen.

▶**N.B**: A major use of inhibitor is in the preservation of monomers during production and storage. Otherwise due to their high reactivity monomer undergoes polymerisation during production, storage & transportation. Before use monomers are freed from distilation or by washing with aqueous NaOH or KOH.

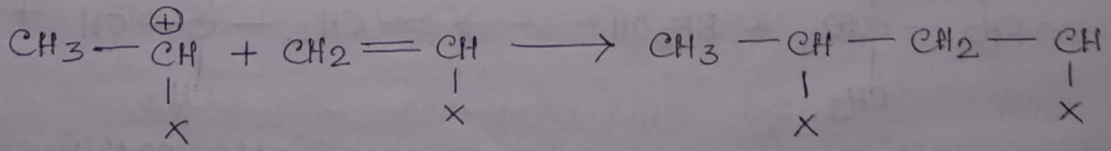
In industry, inhibitors are used for the purpose of arresting the polymerisation beyond a certain conversion to achieve a uniform product, so, they are called "short stops". They are normally added towards the end of the polymerisation.

2) ▶ Ionic polymerisation :

This is a chain polymerisation which initiate through ionic mechanish involving an attack of ion on the π- electron pair of monomer.



$$H^{\oplus} + CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow H-CH_2-\overset{\oplus}{\underset{X}{\underset{|}{CH}}}$$



$$CH_3-\overset{\oplus}{\underset{X}{\underset{|}{CH}}} + CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow CH_3-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}$$

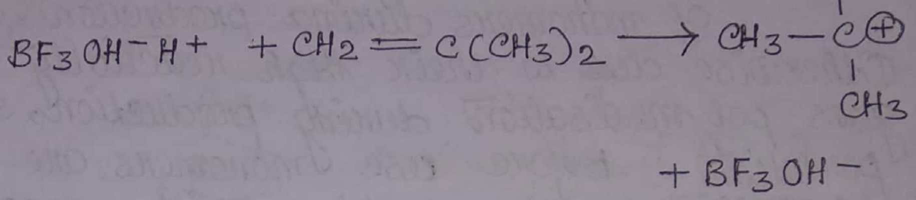
Generally, monomers with e⁻ releasing substituent such as — 1,1-dialkyl, aryl-alkyl, phenyl, vinyl & butadiene are readily susceptable to cationic polymerisation and monomers with e⁻ - withdrawing substituent such as nitrile, carboxyl, ester are readily susceptible to anionic polymerisation.

Cationic polymerisation :

Polymerisation is initiated by a cation. Protonic acid, such as H_2SO_4, $HClO_4$ or Lewis acid e.g BF_3, $SnCl_4$, $AlCl_3$, $AlBr_3$, $TiCl_4$ etc readily induce cationic polymerisation. Here such Lewis acid are called 'catalyst'. Such catalyst become active in presence of cocatalyst such as, water, alcohol, organic acid, alkyl acid or hydrocarbon.

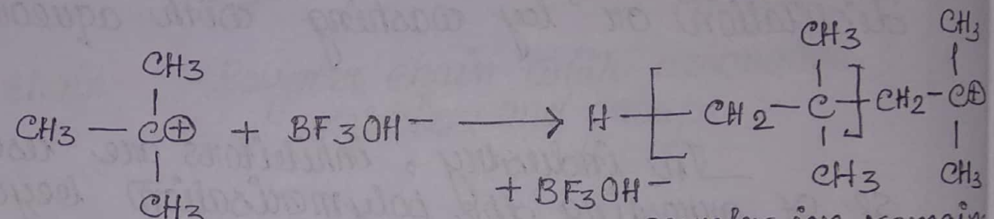
Ex — $BF_3 + H_2O \longrightarrow BF_3OH^- H^+$

Initiation :



$$BF_3OH^-H^+ + CH_2{=}C(CH_3)_2 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + BF_3OH^-$$

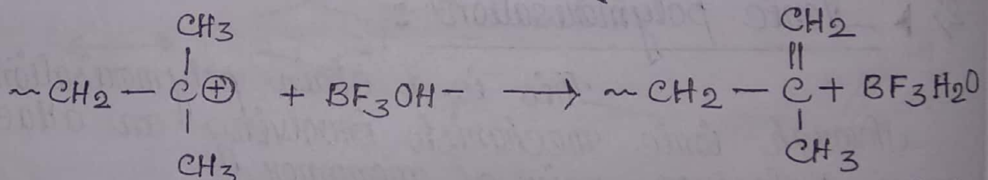
Propagation :



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + BF_3OH^- \longrightarrow H-\left[CH_2-\overset{CH_3}{\underset{CH_3}{C}}\right]-CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + BF_3OH^-$$

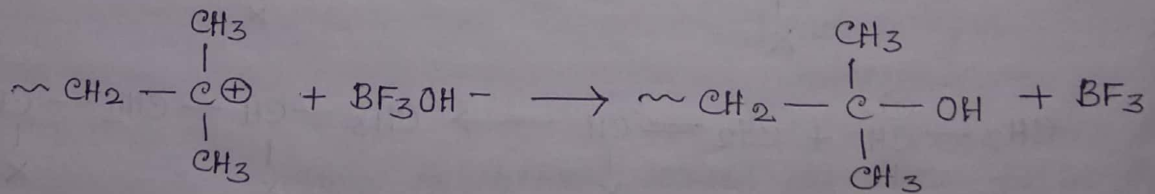
counter ion remains close to the growing chain and helps in solvation & polymerisation.

Termination :



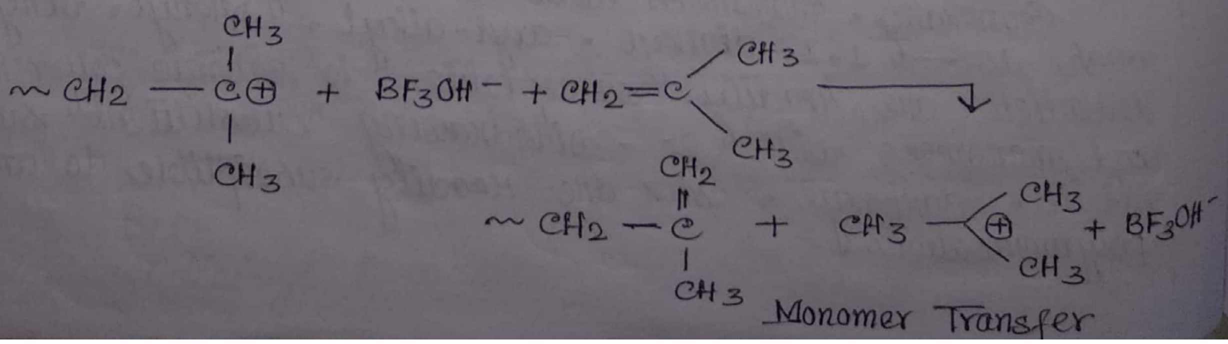
$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + BF_3OH^- \longrightarrow \sim CH_2-\overset{CH_2}{\overset{\|}{\underset{CH_3}{C}}} + BF_3H_2O$$

Proton abstraction



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + BF_3OH^- \longrightarrow \sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OH + BF_3$$

Simple coupling



$$\sim CH_2-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + BF_3OH^- + CH_2{=}C(CH_3)_2 \longrightarrow \sim CH_2-\overset{CH_2}{\overset{\|}{\underset{CH_3}{C}}} + CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + BF_3OH^-$$

Monomer Transfer

N.B: During termination process, proton abstraction can take place, generating $BF_3 \cdot H_2O$. This process of donation of a proton and the reformation of $BF_3 \cdot H_2O$ is called 'ion-pair precipitation'.

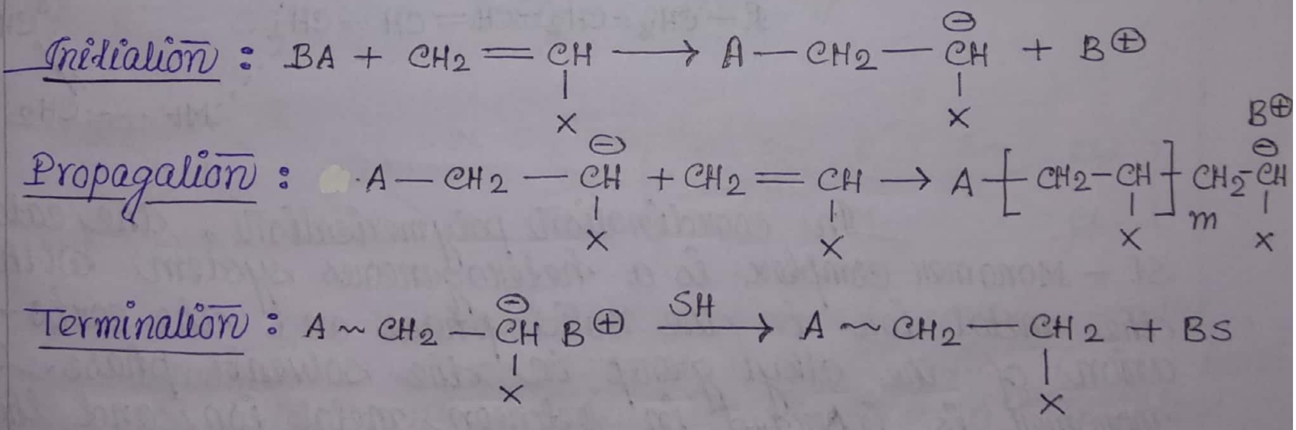
The counter ion BF_3OH^- remains close to the propagating chain through out the chain like a 'watch-dog'.

N.B: BF_3 was found to be ineffective to induce polymerisation of isobutylene when the reactants were taken in a high degree of purity and free from moisture. The catalyst is however very effective in the presence of traces of moisture or similar polar additives as a co-catalyst.

Anionic polymerisation :

Polymerisation is initiated by an anion. Amides, Alkoxide, alkyls and aryls of alkali metals and different Grignard reagent are used as catalyst for anionic polymerisation.

Ex — $BA \rightleftharpoons B^+ + A^-$



Initiation : $BA + CH_2{=}\underset{X}{CH} \longrightarrow A{-}CH_2{-}\underset{X}{\overset{\ominus}{CH}} + B^{\oplus}$

Propagation : $A{-}CH_2{-}\underset{X}{\overset{\ominus}{CH}} + CH_2{=}\underset{X}{CH} \longrightarrow A{+}\Big[CH_2{-}\underset{X}{CH}\Big]_m CH_2{-}\underset{X}{\overset{\ominus}{CH}}\ B^{\oplus}$

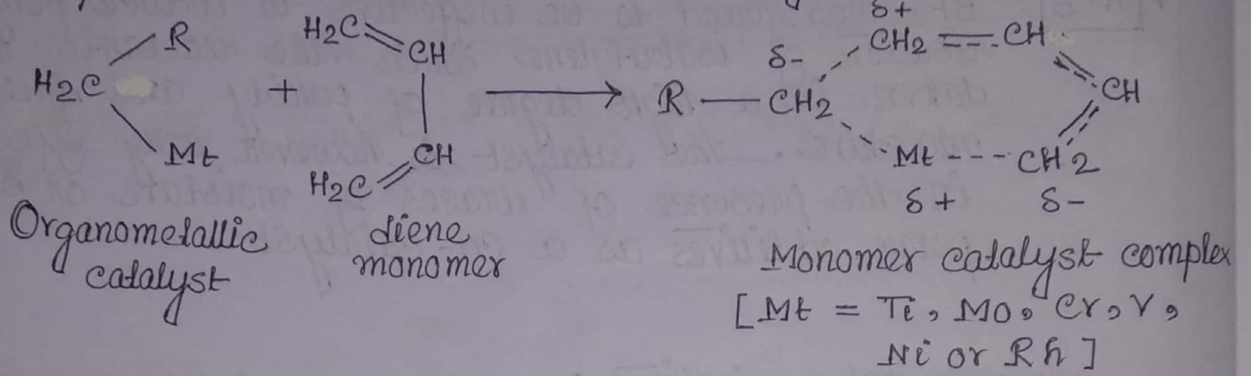
Termination : $A{\sim}CH_2{-}\underset{X}{\overset{\ominus}{CH}}\ B^{\oplus} \xrightarrow{SH} A{\sim}CH_2{-}\underset{X}{CH_2} + BS$

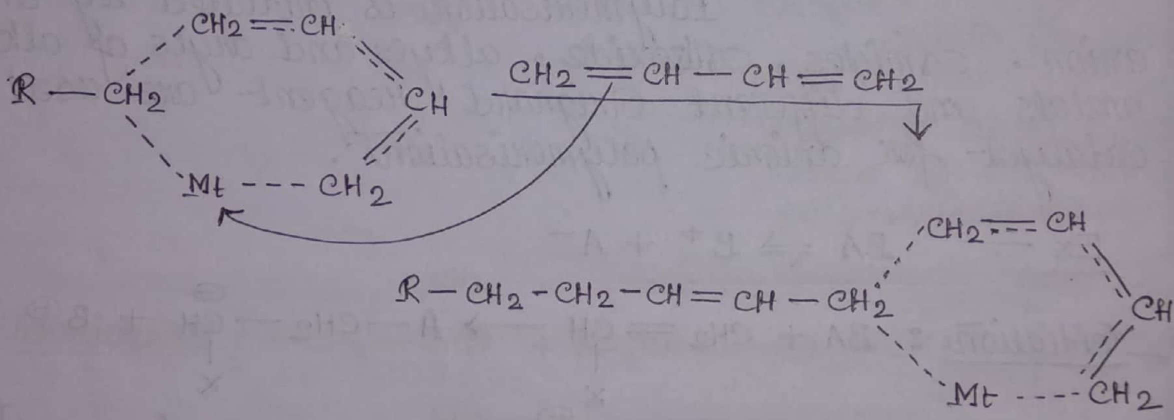
Termination open takes place by chain transfer involving solvent or some other 'additives (SH) used such as water, alcohol etc.

N.B: If the polymerisation is carried out under controlled condition without any impurity, the reaction proceeds till all the monomer is consumed. But the carboanions remain active & can start polymerisation if fresh monomers are added. The polymers produced by such technique are called 'living polymer.' They are alive and keep on growing as long as we supply fresh quantidative monomers. Just as living organism grow as long as food is available.

3. Coordination polymerisation :

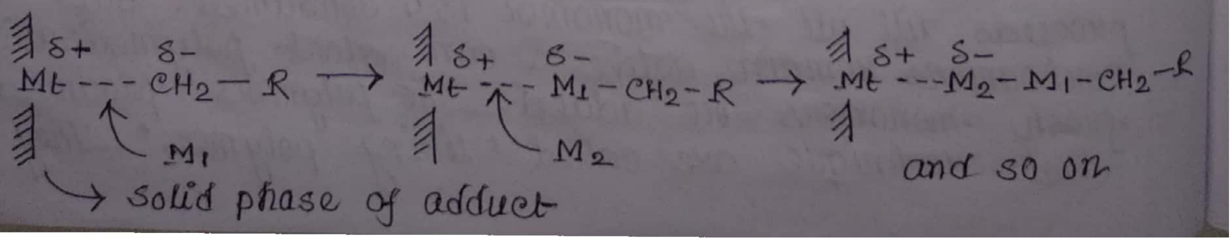
Polymerisation reaction especially of ~~Ol~~ Olefins and dienes, catalysed by organometallic compound are called coordination polymerisation.





In coordination polymerisation, the catalyst – Monomer complex is a heterogeneous system with the metal ion in the solid phase and the carboanion of the alkyl group in the solvent phase. The monomer is inserted in between metal ion and the carboanion with the result that the polymer chain formed is pushed out from the solid catalyst surface.

For these reason co-ordination polymerisation is also known as '*insertion polymerisation*'.



Stereo-regular polymers :

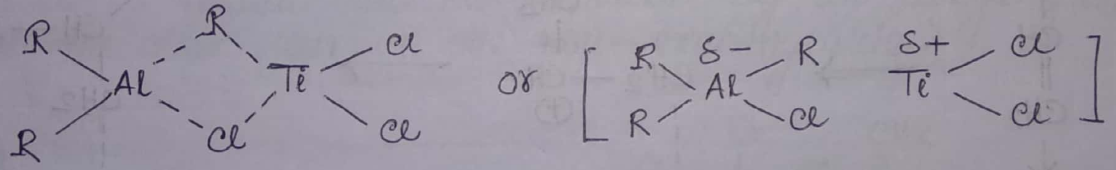
One interesting feature of co-ordination polymerisation is that, in certain catalyst system, the spatial arrangement has a tremendous effect on the spatial orientation of the incoming monomer and also the manner in which the monomer is inserted. This specific spatial arrangement imparts stereo-regularity to the polymer formed and is called stereo-regular polymer. By choosing a proper catalyst / solvent system, it is possible to formulate highly stereo-regular polymer. One well-known example is → Ziegler-Natta catalyst.

Ziegler - Natta catalyst :

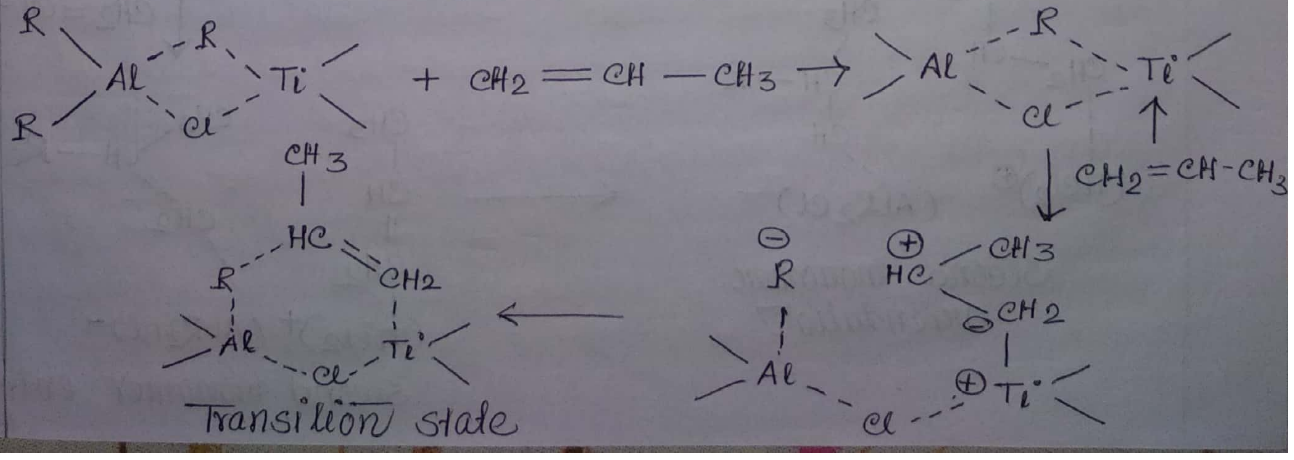
It is composed of two components, catalyst and co-catalyst. The catalyst are halides of 4-8 group elements and the co-catalyst are organometallic compound such as alkyls, aryls, halides and hydrides of group 1-4 metal. Examples are $AlEt_3$ or $AlEt_2Cl$ in combination with $TiCl_3$ or $TiCl_4$.

Bi-metallic mechanism :

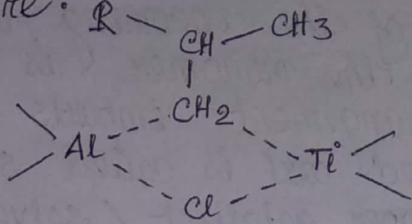
When the catalyst and cocatalyst components are mixed, there occur a chemisorption of AlR_3 on $TiCl_3$ solid surface, resulting in the formation of e^- – defficient bridge complex.



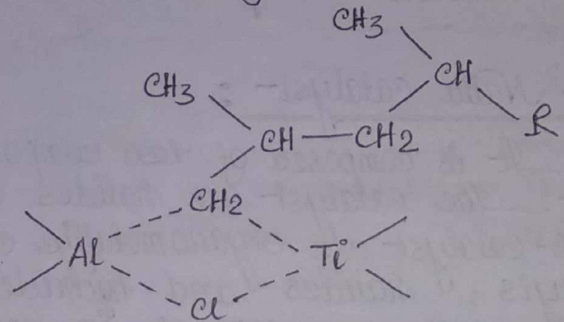
This complex now acts as the active centre, the monomer is then attracted towards the Ti – C bond in the active centre, when it forms a π - complex with the Ti - ion followed by opening of R–Ti bond.



Ti- ion attract the π- electron pair of monomer, forms a σ- bond while the counter ion attracts the e^- - defficient centre of the monomer. Thus monomer is inserted in the T.S ring structure. ~~It~~ ~~Now~~ the T.S is now gives rise to the chain growth at the M—C bond, regenerating the active centre.

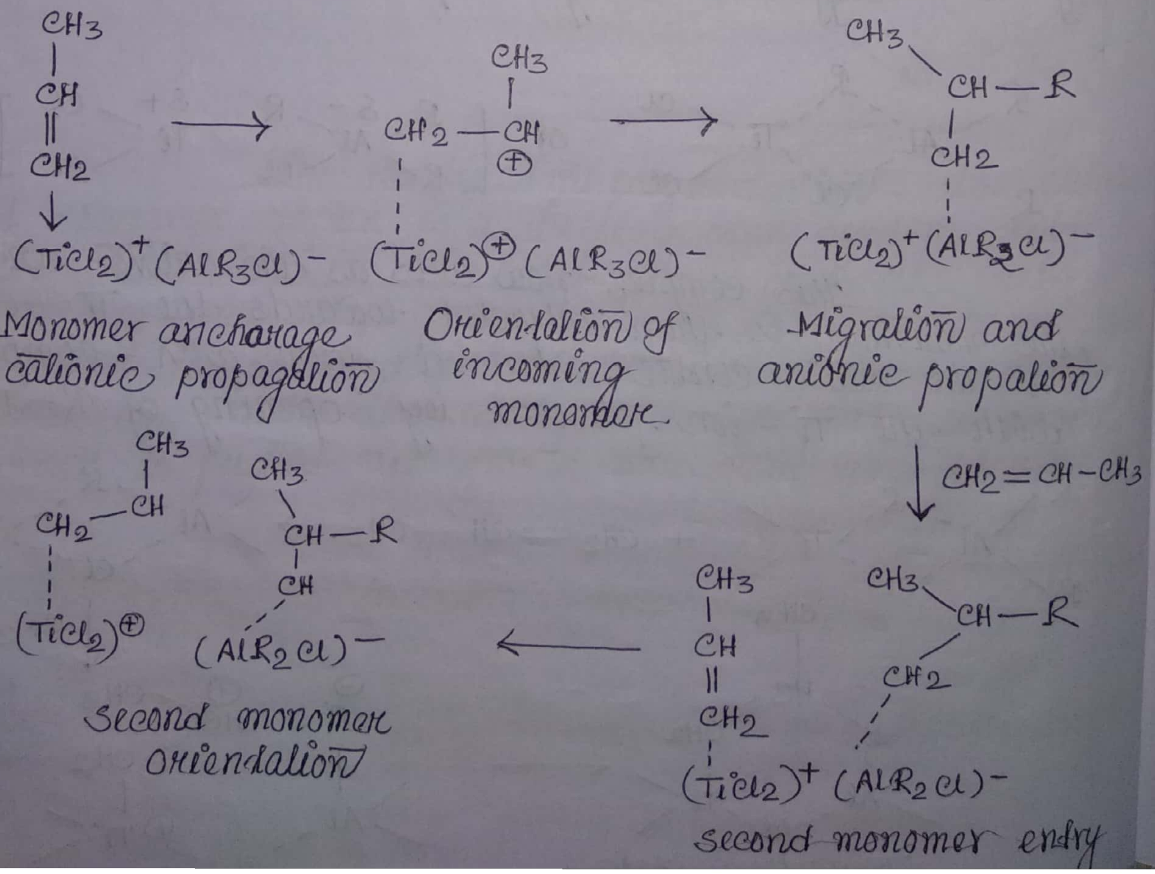


For the addition of 2nd monomer, we get the structure ———



The orientation of the substituent group of the monomer is always taken from the metal- ion ~~ed~~ end, resulting in a stereoregulated polymer.

Another way to represent bimetallic mechanism:



Monomer ancharage cationic propagation

Orientation of incoming monomere

Migration and anionic propation

second monomer entry

Second monomer oriendation