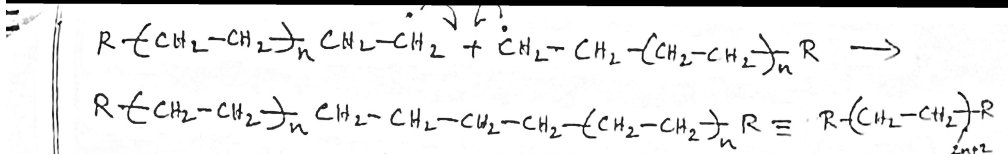


$$R\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}\dot{C}H_2 + \dot{C}H_2\text{-}CH_2\text{-}(CH_2\text{-}CH_2)_n\text{-}R \longrightarrow$$

$$R\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}(CH_2\text{-}CH_2)_n\text{-}R \equiv R\text{-}(CH_2\text{-}CH_2)_{2n+2}\text{-}R$$

Dead Polymer (will not grow further)

(ii) Disproportionation.

Here, hydrogen atom of one radical centre is transferred to another radical centre so that to give unsaturated polymer + saturated polymer.

$$R\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}\dot{C}H_2 + \dot{C}H_2\text{-}\underset{H}{CH}\text{-}(CH_2\text{-}CH_2)_n\text{-}R \longrightarrow$$

$$R\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_2\text{-}CH_3 + CH_2=CH\text{-}(CH_2\text{-}CH_2)_n\text{-}R.$$

Saturated polymer — unsaturated polymer.

(2) Mechanism of cationic Polymerisation.

This type of Polymerisation occurs in the monomers having electron releasing groups. The catalysts used are acids such as H_2SO_4, HF etc., or Lewis acids, such as $AlCl_3$, BF_3, $SnCl_4$ etc., with the co-catalyst, water or methanol in small amounts (e.g., $BF_3 + H_2O \longrightarrow HOBF_3^- H^+$)

(i) chain-initiation step

Due to the presence of electron donating groups, polarity is created along the double bond and H^+ (proton ion) attach itself to the negatively charged carbon atom and finally carbocation (carbonium ion) is formed.

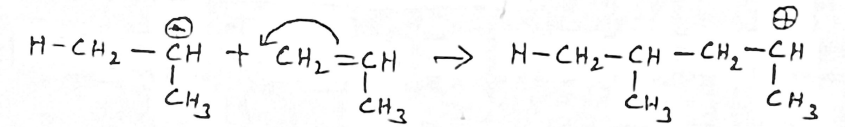
(e.g.,) $H_2SO_4 \longrightarrow H^+ + HSO_4^-$

(Initiator) (proton)

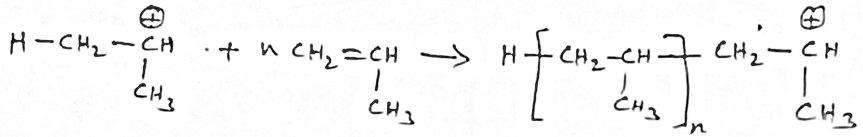
$$H^+ + CH_2=\underset{CH_3}{CH} \longrightarrow CH_3-\overset{\oplus}{\underset{CH_3}{CH}}$$

(monomer) (carbonium ion)

(ii) chain - Propagation step

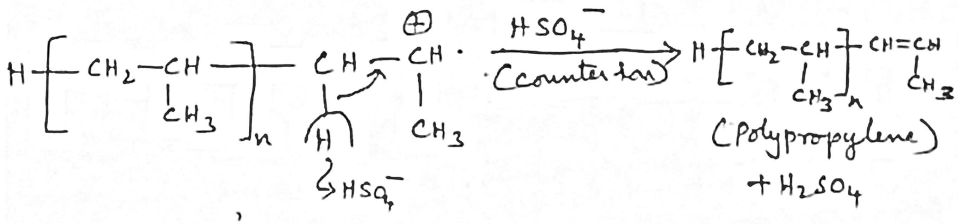


(A new carbonium ion)



iii) chain - Termination step

The growth of the chain is stopped by combination with an anion or by the loss of a proton.



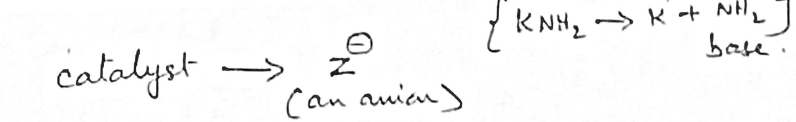
(Polypropylene)

$+ H_2SO_4$

(3) Mechanism of Anionic Polymerisation.

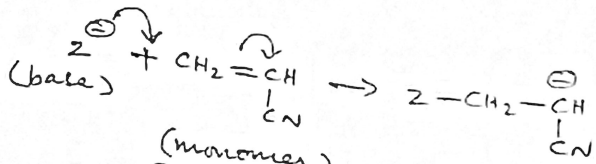
This type of polymerisation reaction takes place when electron withdrawing groups such as chlorine, cyanide etc., are present in the monomer. The catalyst used are bases, like $LiNH_2$, KNH_2, $NaNH_2$ etc., (sodamide (negatively charged nitrogen is

i) chain - Initiation step



(an anion)

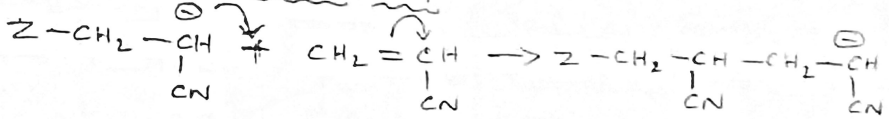
{ $KNH_2 \rightarrow K^+ + \overset{\ominus}{NH_2}$ } base.

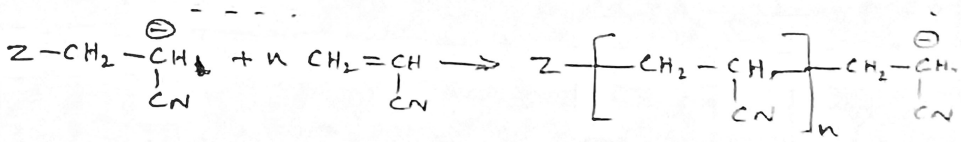


(base) (monomer) (acrylonitrile) A new anion (carbanion)

Because of the electron withdrawing cyanide group, slight polarity is created in the monomer, thereby $:Z^{\ominus}$ attaches itself to the carbon atom which is deficient of e⁻s. Finally carbanion is formed.

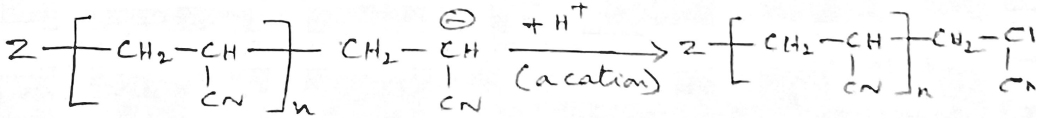
(ii) Chain-propagation step





(iii) Chain-Termination step

The growth of the chain is stopped by the attachment of protons.



(a cation)

Cpolyacrylonitrile

(4) Ziegler - Natta Polymerisation or co-ordination Polymerisation (Mechanism)

co-ordination polymerisation was first proposed for the addition polymerization of ethylene and propylene with Ziegler - Natta catalysts

A co-ordination polymer is defined as a polymeric substance containing a coordination compound or metal complex in its repeat unit.

Polymerisation reactions of alkenes are generally catalysed by Zeigler - Natta catalyst. Ziegler - Natta catalyst is the combination of transition metal halide and organometallic compounds. The important Ziegler - Natta catalyst is formed from ($TiCl_4 + (C_2H_5)_3Al$)

The $AlEt_3$ reduces the $TiCl_4$ to $TiCl_3$ and replaces some of the surface chlorine atoms with ethyl groups. The rate of polymerisation is proportional to the total amount of $TiCl_3$ and the pressure of the olefin and is independent of the $AlEt_3$ concentration. A critical step in the process is believed to be the interposition of an olefin molecule between the Ti atom and an alkyl group.

The octahedrally coordinated Titanium atom at a surface site, coordinated to only four chlorine atoms. The fifth octahedral site is occupied by an alkyl gp, and the sixth site is available for the olefin. The olefin forms a 'σ' bond to the metal using its filled π orbital.

In a concerted step, the alkyl gp breaks its bond to the metal and forms a bond to one of the olefin carbon atoms, as the other olefin carbon atom becomes attached to the metal.

structure of Ziegler-Natta catalyst

~~c) Chain~~.

M-ech: It appears to occur with the insertion of alkene molecule into the bond between metal and the alkyl gp of the catalyst.

a) chain initiation step:

$$Cat-Ti-R + CH_2=CH_2 \rightarrow Cat-Ti-CH_2-CH_2-R$$

ethylene

This Ti-C bond is the active centre from where the propagation starts.

b) chain propagation step

The monomers are inserted between the Ti-C bond and the chain grows.

$$Cat-Ti-CH_2-CH_2-R + CH_2=CH_2 \rightarrow Cat-Ti-CH_2-CH_2-CH_2-CH_2-R$$

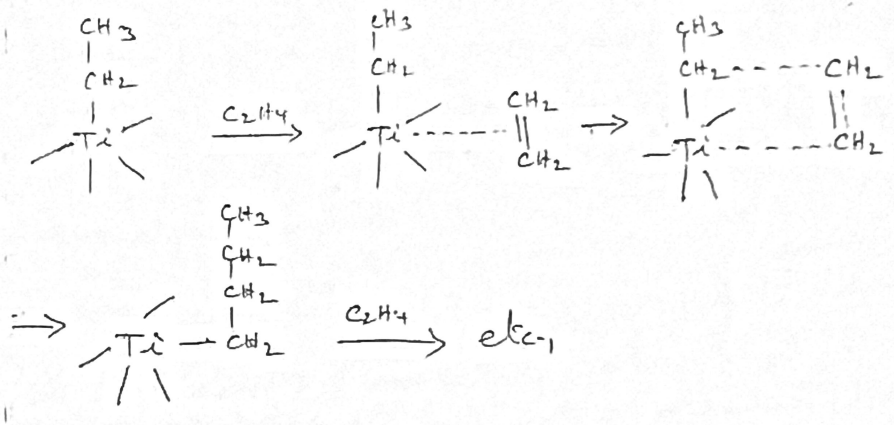
$$\therefore Cat-Ti-CH_2-CH_2-R + n\,CH_2=CH_2 \rightarrow Cat-Ti-CH_2-CH_2-\{CH_2-CH_2\}_n-R$$

c) chain-Termination step (with active hydrogen compound)

$$Cat-Ti(Cl,H)-\{CH_2-CH_2\}_n-R \xrightarrow{HCl}$$

$$Cat-Ti-Cl + CH_3-CH_2-\{CH_2-CH_2\}_n-R$$

polymer



The stereospecific and stereoregular polymers are obtained. Because of non-equivalence of the coordination sites of olefin and ~~active~~ alkyl group at the active titanium center, the growing alkyl gp moves back to its original position after each insertion of a new monomer.

Advantages of Zeigler-Natta Polymerisation.

① Zeigler-Natta catalyst is used in the preparation of Polyethylene, Polypropylene, polydienes.

② This is helpful to prepare stereospecific polymers.

③ using ordinary catalysts, the desired polymers cannot be prepared. But using Zeigler-Natta catalysts, the desired polymers (i.e., atactic or isotactic or syndiotactic) are produced.