vinyl polymerisation

or

CHEMISTRY OF POLY

or

Addition polymerisation →

"Addition polymerisation is also known as chain polymerisation"

⇒ This type of polymerisation involve the self addition of normal unsaturated molecule without loss of any small molecule to give a single giant molecule.

∴ This polymerisation is also known as vinyl polymerisation.

These polymerisation pass through successive stage of Initiation, propagation, termination common to chain reactants.

free radical — Ionic — Co-ordinate

(1) FREE RADICAL ADDITION POLYMERISATION ⇒

Initiators: Initiators are thermally unstable compounds which on heating easily decompose into free radicals.

Exa: Peroxides, azocompound, ~~polyesters~~, H_2O_2

$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R$

Imp ⇒ Benzoyl peroxide is a commonly used initiator

$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5$ ⟶ Heat

$$2\,C_6H_5-\overset{O}{\overset{\|}{C}}-O^{\cdot} \downarrow$$

$$2\,C_6H_5^{\cdot} + 2CO_2$$

(Phenyl free radical)

gmp → Decomposition of H_2O_2 in the presence of Fe^{+2} ions to form OH^-, Fe^{+3}, $OH^{\cdot}$ ... such redox initiators are termed redox polymerisation.

$$H-O-O-H + Fe^{+2} \longrightarrow HO^{\cdot} + HO^- + Fe^{+3}$$

The free radical addition polymerisation involves process initiation, chain growth and chain termination.

(i) Initiation step → A free radical contains a lone or unpaired electron which always looks for another lone electron to couple with it, in order to get stabilised.

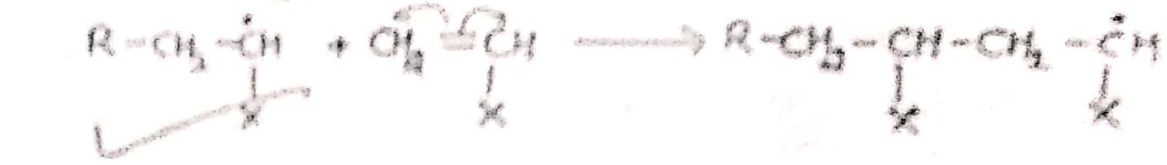
The free radical $R^{\cdot}$ attacks the double bond of the monomer molecules.

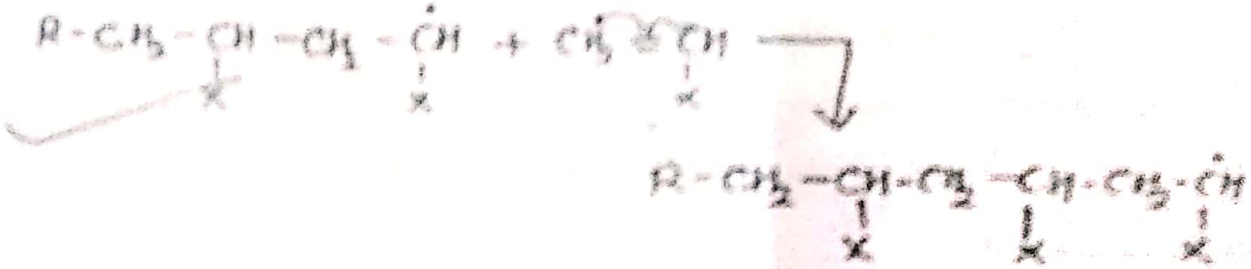
$$CH_2=CHX + R^{\cdot} \longrightarrow R-CH_2\dot{C}HX$$

The free radical attacks on the monomer, initiating polymerisation is an exothermic process and F.R. formation by initiator decomposition is an endothermic process.

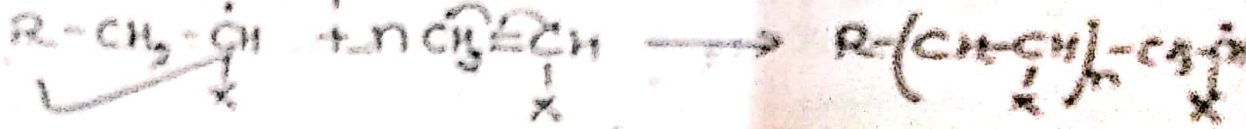
(ii) Propagation step ⇒ The new free radical so formed adds to another molecule of monomer to form another free radical, which further adds to another fresh molecule to form another free radical, ~~which~~

and so on.





overall propagation

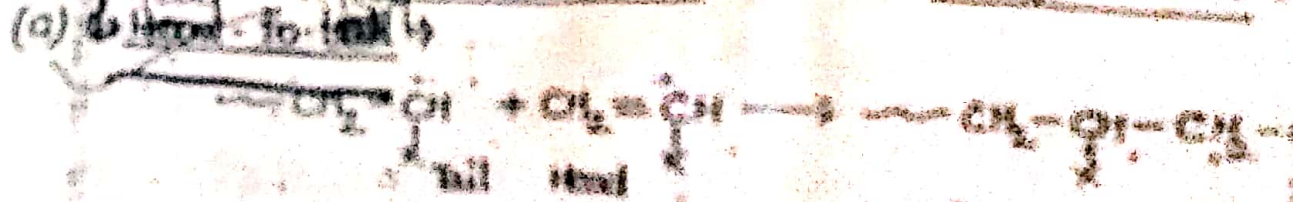


n is denoted the number of monomer units added up in the chain growth.

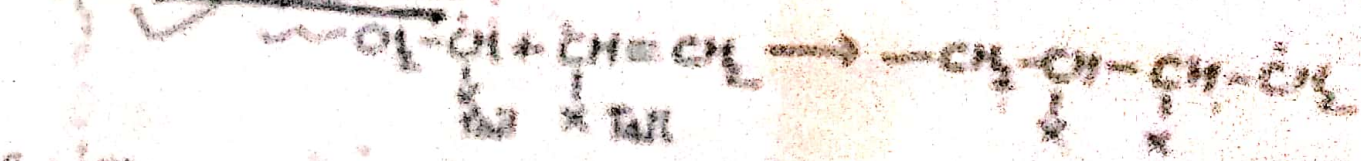
The mode of addition of the incoming monomer to the growing chain can be of the head-to-tail, tail to tail, head to head or tail to head type.

Assuming $-CH_2$ part as head and $-CH$ part as tail

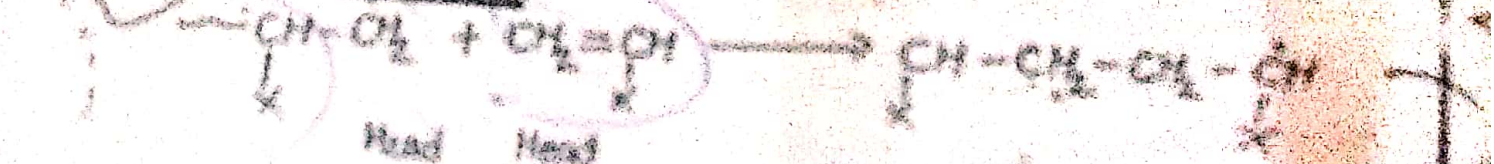
(a) Head-to-tail



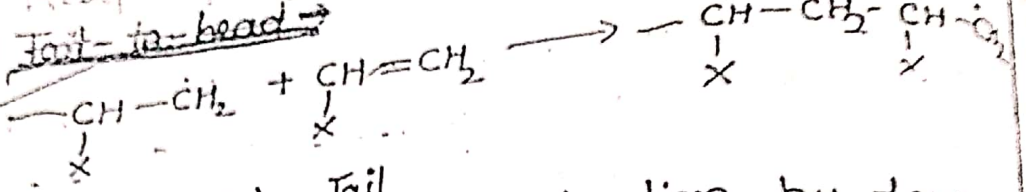
(b) Tail-to-tail



(c) Head-to-Head

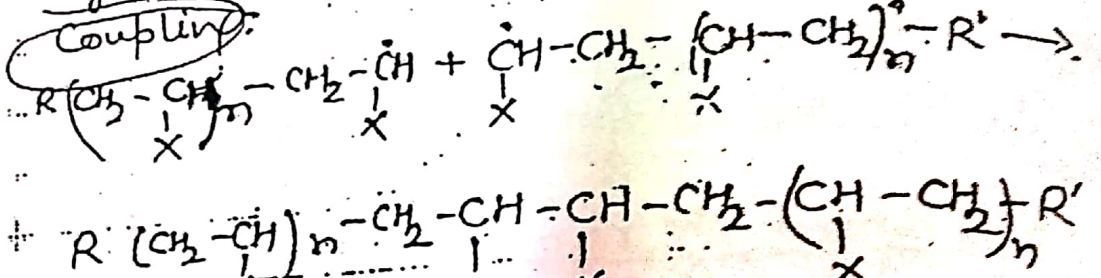


(a) Tail-to-head

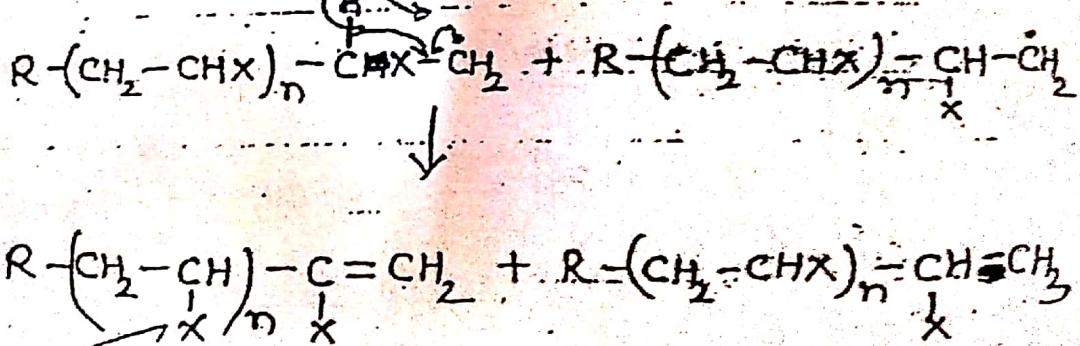


(iii) Termination step ⇒ Termination by four types:

(a) by coupling ⇒ The step in which two large growing chains come close and couple together to stop the chain reaction is called coupling.



(b) by disproportionation ⇒ The chain that loses hydrogen atom, stabilises itself by the formation of a double bond. This process is called disproportionation.



(c) by chain transfer ⇒ In the case of transfer reaction, while the growth of one polymer chain is stoped or arrested, forming a dead polymer, there is a simultaneous generation of a new free radical capable of initiating a fresh

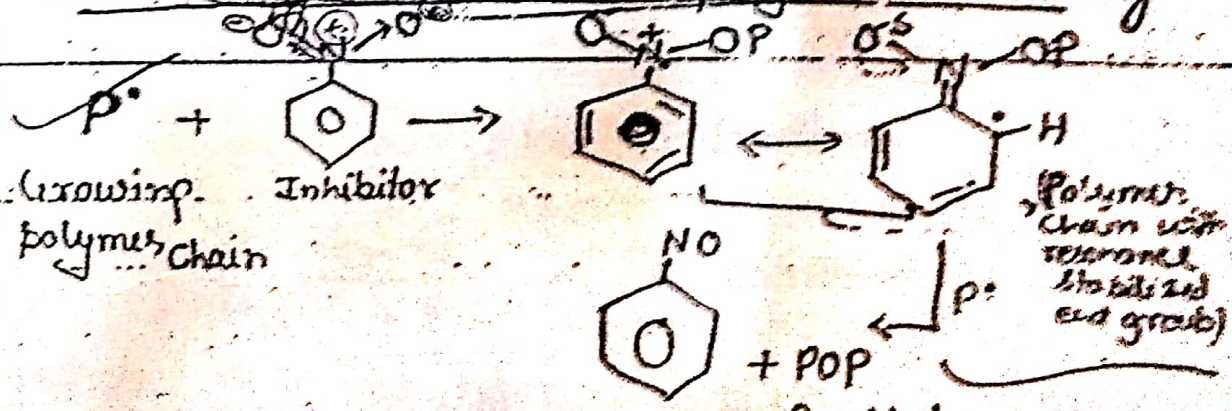
polymer chain growth. This reaction takes place by the abstraction of a hydrogen atom or some other atom from the initiator, monomer or polymer or from any other species present in the system, including the solvent.

$$R-(CH_2-\underset{X}{CH})_n-CH_2-\dot{\underset{X}{C}}H + R'H \longrightarrow R-(CH_2-\underset{X}{CH})_n-CH_2-\underset{X}{CH_2} + R'^{\bullet}$$

free radical

(d) Inhibitors: Inhibitors are chemicals substances capable of inhibiting or killing the chain growth by combining with the active free-radicals and forming either stable products or inactive free radicals.

Exa: Hydroquinone, nitrobenzene, dinitrobenzene, benzothiazine are some of the inhibitors customarily used in the polymer industry.



⇒ Inhibitors are used to arrest the polymerisation at some specific point in order to get a uniform product and to avoid cross linking. When used for this purpose inhibitors are called "short stops".