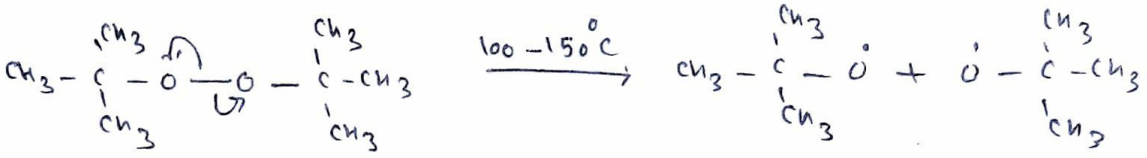
Free radical Polymerisation

Most of the commercial addition polymers are vinyl polymers [$CH_2 = CH - G$] where G = H, CH_3, C_6H_5, Cl, CN, COOR etc.).

This type of polymerization is carried out by heating the monomer with a very small of radical initiator or by subjecting the monomer to ultraviolet light.

tert. Butyl peroxide, benzoyl peroxide are commonly used initiators because they decompose under mild conditions to form radicals.

ex



tert. Butyl peroxide — tert. Butoxide free radical

Benzoyloxy radical

Free radical polymerization occurs through —

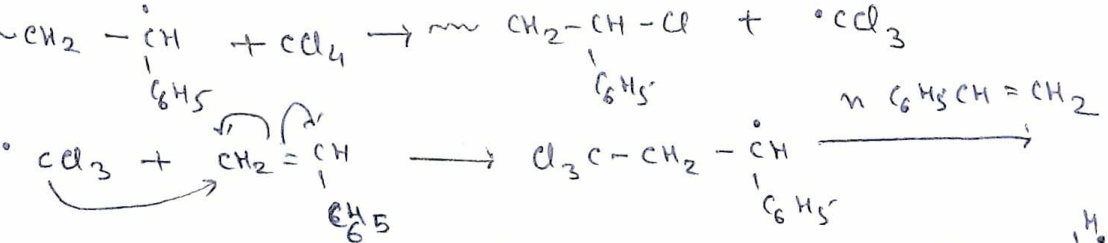
1- Chain initiation 2. chain propagation 3. chain termination

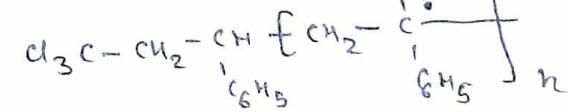
many alkenes or substituted alkenes such as propylene, vinyl chloride, Styrene, acrylonitrile, vinyl acetate etc. undergo radical polymerization.

Termination step involves either combination (coupling) or disproportionation of growing radical chains.

However growth of the original polymer chain may also get terminated or interrupted in presence of certain compds such as CCl_4

It will terminate the original polymer chain and a new radical will be produced to start a new polymer chain.

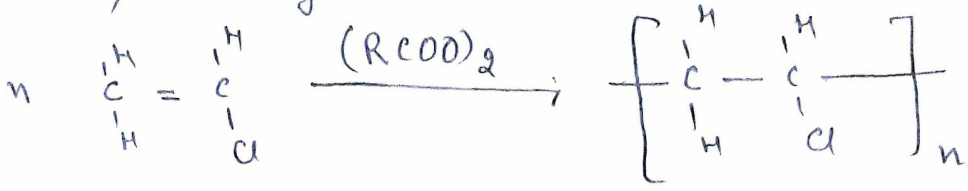




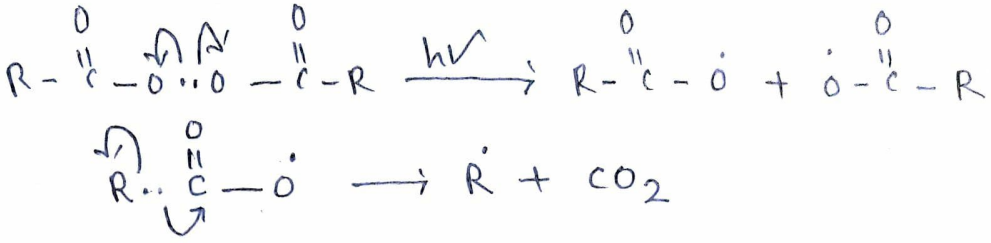
There are certain impurities which inhibits the process of polymerization (inhibitors) ex – phenols, quinones, amines etc.

, radical couple with polymer radical and Further reaction stops.

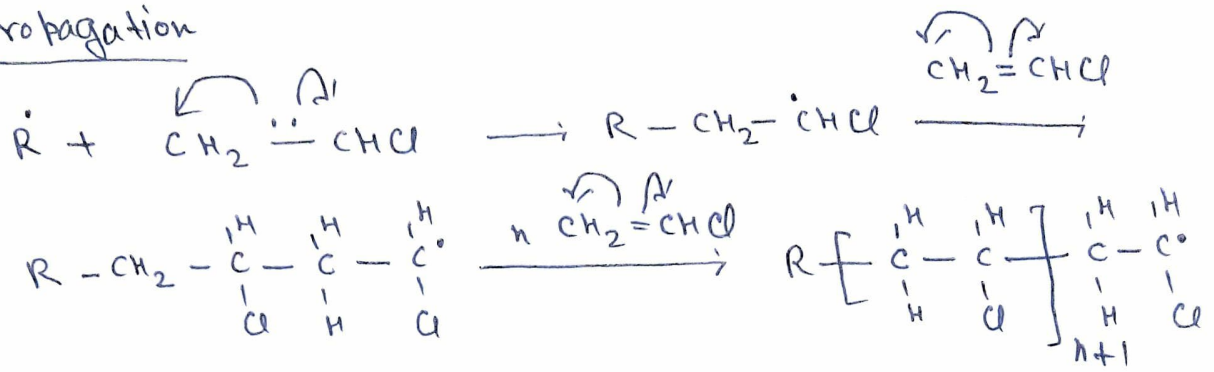
Mechanism :- Mechanism of free radical polymerization may be understood by following example –



Chain initiation

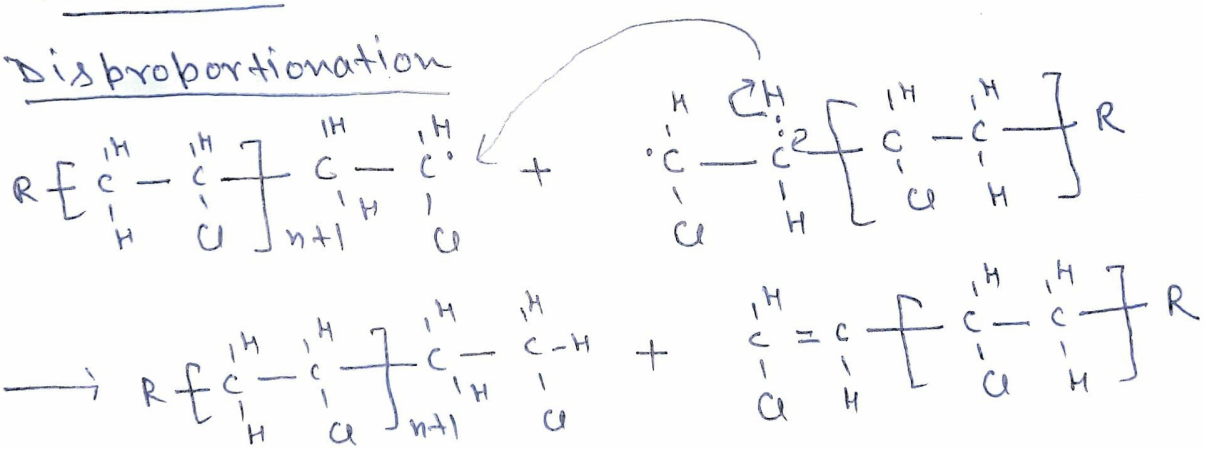


Chain propagation



Chain termination

(a) **Disproportionation**



(b) **Combination (Coupling)**