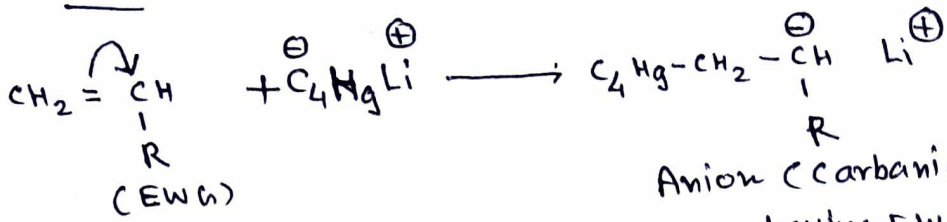
Anionic addition polymerisation

Anionic polymerisation is initiated by strong base such as n-BuLi (normal butyl lithium) and Lithium amide ($LiNH_2$), $NaNH_2$ etc.

the general mechanism of anionic addition polymerisation may be given as -

Chain initiation step



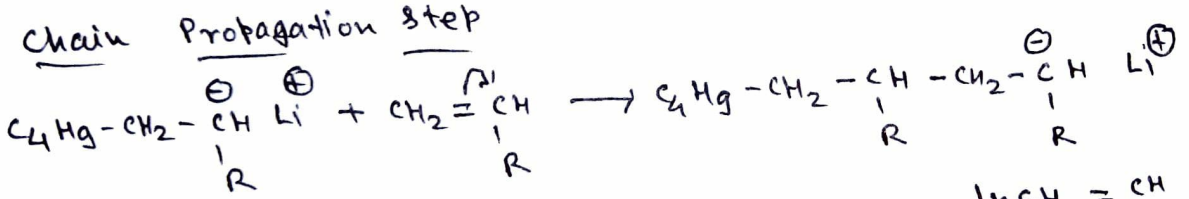
(EWG) Anion (carbanion)

Anionic polymerisation is more favourable with the monomers having EWG (ex- acrylonitrile $CH_2=CHCN$, $C_6H_5CH=CH_2$ Styrene) because EWG help in the stabilisation of carbanion.

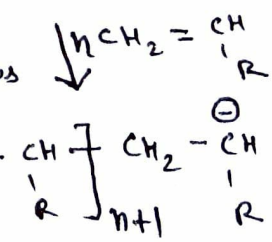
Reactivity of some alkenes towards anionic polymerisation may be given as -

$CN CH=CH_2 > F_2C=CH_2 > C_6H_5-CH=CH_2 > CH_3CH=CH_2$

Chain Propagation step



In anionic polymerisation only initiation & propagation steps are significant, anionic species obtained in propagation steps are quite stable and kept as such for many-many years.



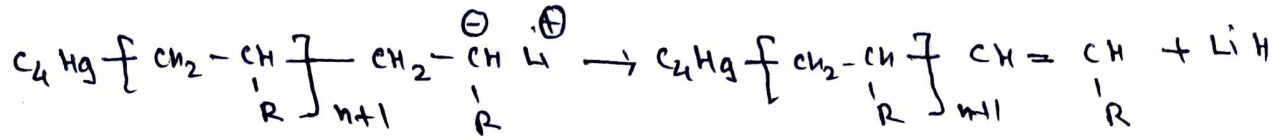
this macromolecular anionic species are called living polymers because this anionic species can resume propagation with same or different monomer.

macromolecular anionic species [Living polymers]

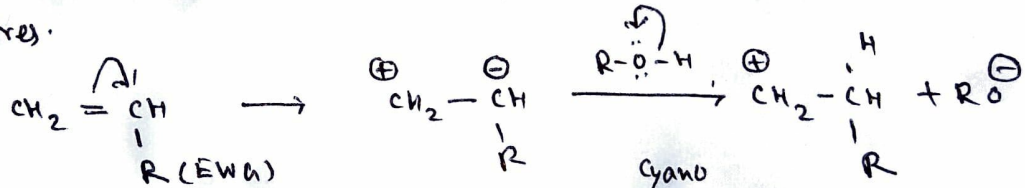
So, Spontaneous termination reactions are effectively absent in no. of anionic polymerisations.

Chain termination step :-

Termination occurs by a $H^{\ominus}$ (hydride ion) transfer or by the action of reactive centre with solvents or with functional group of the monomer.



1. Anionic polymerisation is usually carried out in the presence of non-polar solvents. Polar protic solvents are acidic, enough to destroy carbanionic active centres.



2. Alkenes containing EWG like acrylonitrile, methyl acrylate ($CH_2 = C(CN)$, $-COOCH_3$), Styrene etc. can be polymerized under anionic conditions although free radical polymerization is commercially preferred.