

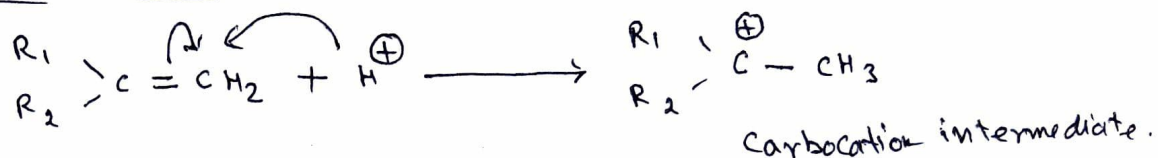
Ionic Vinyl Polymerization

Cationic Addition Polymerization

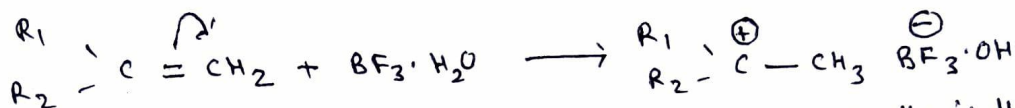
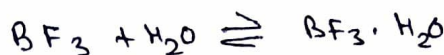
Cationic polymerization is initiated by Lewis acids, such as BF_3 , AlCl_3 , TiCl_4 , SnCl_4 , etc. in presence of trace of water (co-catalyst) or in presence of protonic acid such as H_2SO_4 .

The general mechanism of this type of polymerization may be given as-

Chain initiation step

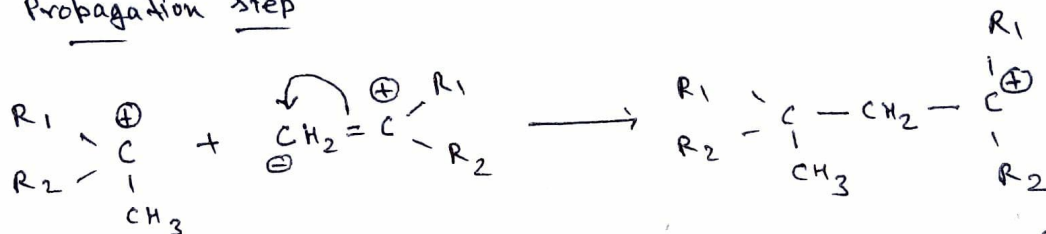


or

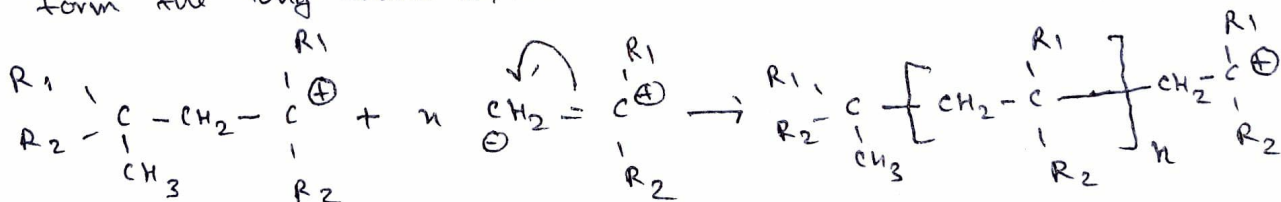


- Ⓐ Greater the stability of the carbocation intermediate, more facile is the cationic polymerisation.
- Ⓑ Thus alkenes containing EDG (electron donating group) are preferably polymerized under cationic conditions although free radical polymerization can also occur.
- Ⓒ Monomers such as vinyl chloride, vinyl cyanide with contain EWG do not polymerize well under these conditions because EWG, destabilises the carbocation intermediate.

Chain Propagation step

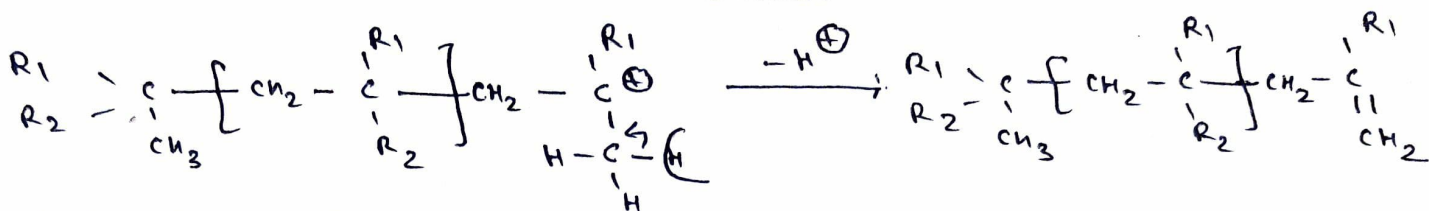


The step repeat itself several times to continue the polymer chain to form the long chain polymer.



Chain termination step

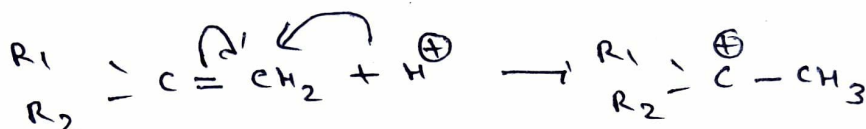
It usually occurs by transfer of H^+ (proton) to base or transfer to monomer.



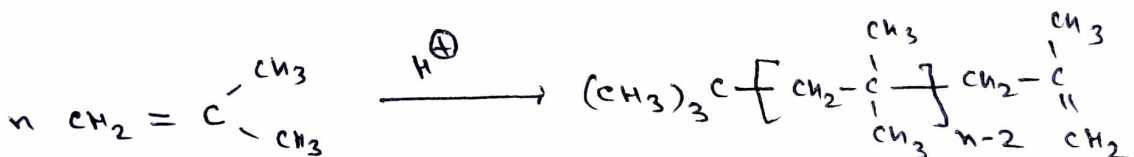
(where $R_2 = CH_3$)



or



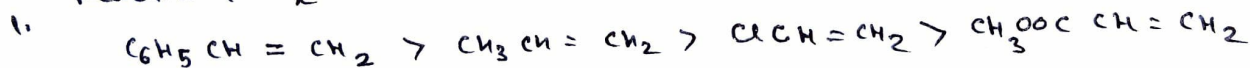
Example-



Isobutylene

Poly isobutylene
(used for making adhesives)

some
Reactivity of alkenes towards cationic polymerization may be given as -



2. The essential feature of cationic polymerization is that they take place at very high rates even at very low temperature.

3. Polymers obtained by cationic polymerization have very low molecular weights because of transfer reaction.

4. The low molecular weight polymers can be used as lubricants, coating materials and softners.

5. Some monomers isomerize during cationic polymerisation (due to rearrangement in carbocation). As a result, in the polymer, repeating unit is not the same as that of monomer. Isomerisation is more common in cationic polymerisation than in free radical polymerisation because carbocation rearranges easily.