

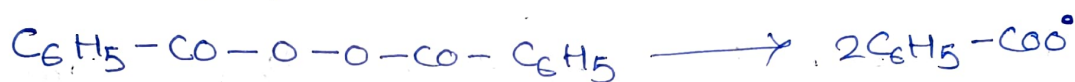
\* Mechanism of radical chain polymerisation

1. Chain Initiation.

(i) Decomposition of initiator to produce free radical.



For example,

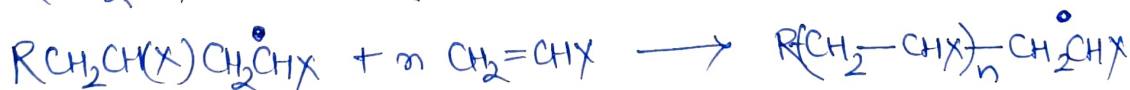


(ii) Addition of the free radical to the monomer with the generation of another radical



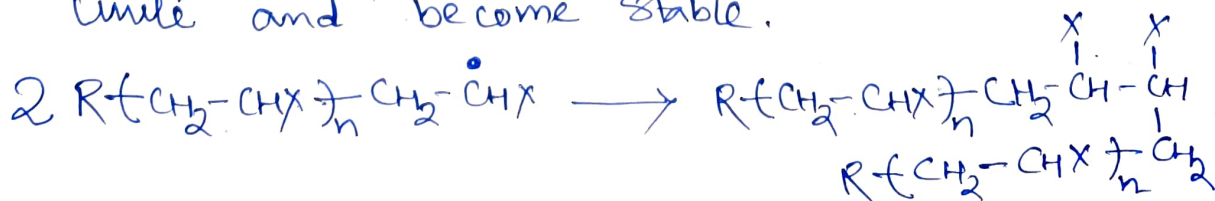
2. Chain Propagation.

The radical site at the first monomer attacks a fresh monomer molecule and the chain continues. So on.

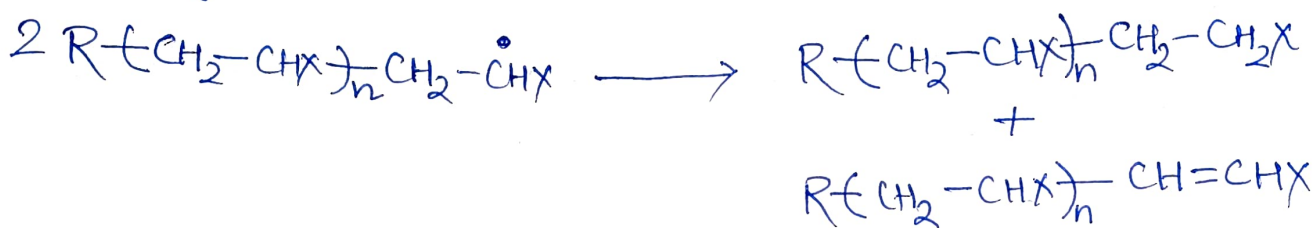


3. Chain Termination.

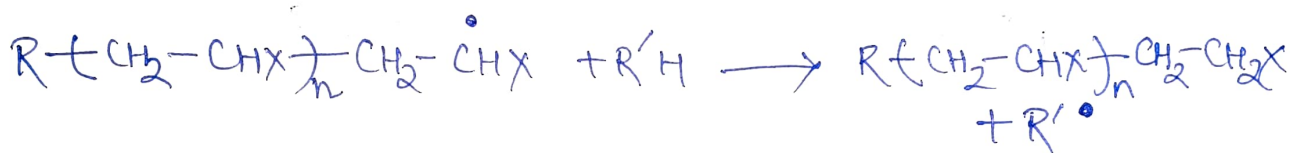
(i) Termination by coupling: Two growing chains unite and become stable.



(ii) Termination by disproportionation. One H atom from one growing chain is abstracted by other growing chain.

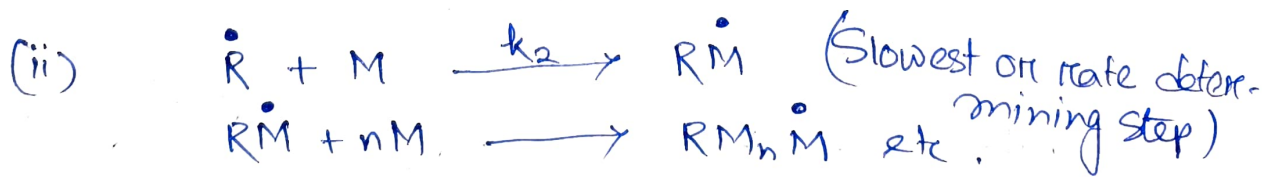


(iii) Chain Transfer. Growth of a chain is stopped by abstraction of H or other atom from the initiator, monomer, or polymer (say R'H) with concurrent generation of a new radical.



### Kinetics of radical chain polymerisation

Let us consider rate constants  $k_1$ ,  $k_2$  and  $k_3$  for chain initiation, propagation and termination steps respectively.



$$\frac{d[R^\bullet]}{dt} = k_1 [I]$$

$$- \frac{d[M]}{dt} = k_2 [R^\bullet] [M] \quad (\text{r.d.s})$$

$$- \frac{d[R^\bullet]}{dt} = k_3 [R^\bullet]^2$$

Now, if we apply steady state approximation to the free radical  $R^\bullet$ ,

$$k_1 [I] = k_3 [R^\bullet]^2$$

$$\Rightarrow [R^\bullet] = \left( \frac{k_1}{k_3} [I] \right)^{1/2}$$

Putting this value to the rate of the slowest step, i.e., chain propagation

$$\begin{aligned} - \frac{d[M]}{dt} &= \frac{k_1^{1/2} k_2}{k_3^{1/2}} [I]^{1/2} [M] \\ &= k [I]^{1/2} [M] \end{aligned}$$

### Kinetic chain length

$\bar{n}$  is defined by average number of monomere molecules consumed by each effective free radical generated by the initiator

$$\bar{n} = \frac{\text{Rate of Propagation}}{\text{Rate of Initiation}} = \frac{\text{Rate of Propagation}}{\text{Rate of termination}}$$

$$= \frac{k_1^{1/2} k_2 [I]^{1/2} [M]}{k_3 [I]}$$

$$= \frac{k_2 [M]}{(k_1 k_3 [I])^{1/2}}$$

## Average degree of Polymerisation

- (i)  $\overline{D}_p = 28$  if termination occurs by coupling  
 (ii)  $\overline{D}_p = 8$  if termination occurs by disproportionation.

## \* Mechanism of Cationic Chain Polymerisation

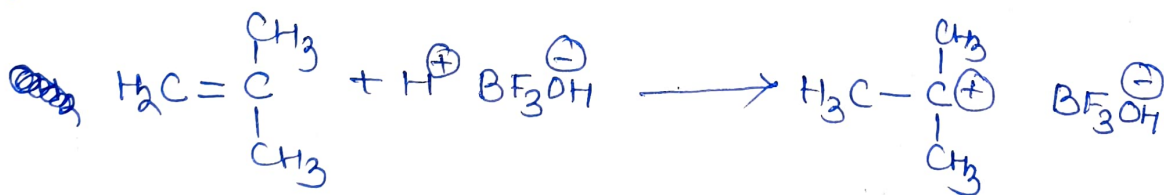
\* Monomers with electron releasing substituents undergo cationic polymerisation.

\* Acids: Protic or Lewis act as initiator.  
 Eg.  $H_2SO_4$ ,  $HClO_4$ ,  $BF_3$ ,  $SnCl_4$  etc.

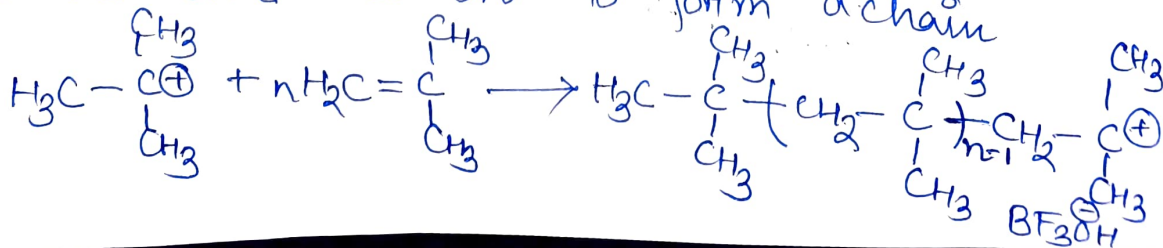
1. Initiation: Strong acids (or, catalyst eg.  $BF_3$ ) in presence of water form hydrates which exist as ion-pair.



$H^+$  acts as initiating cationic species and  $[BF_3OH]^-$  is counter ion.

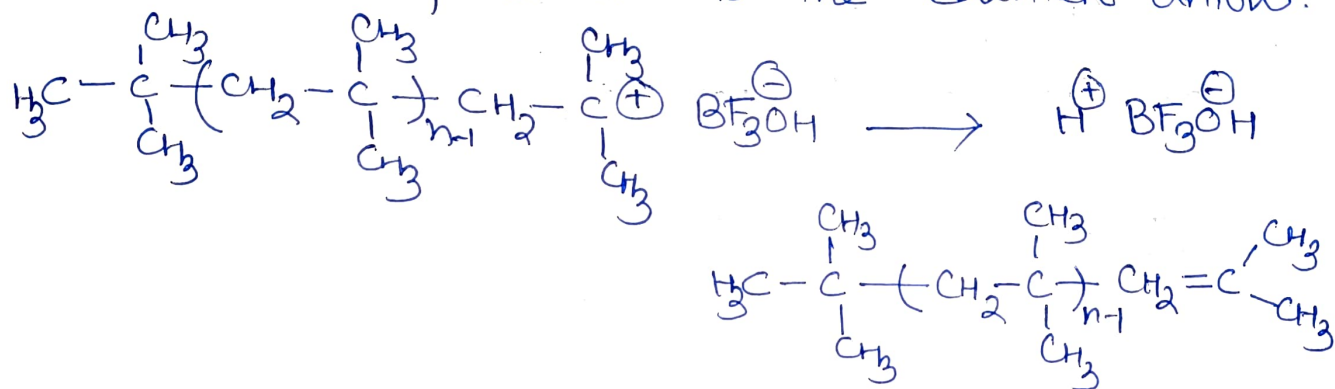


2. Propagation. The carbocation attacks another monomere and so on to form a chain

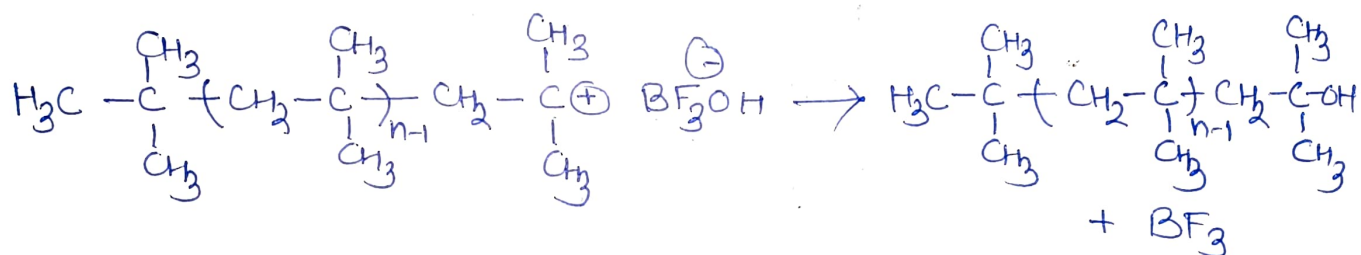


### 3. Termination.

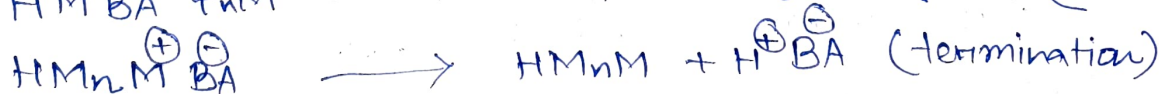
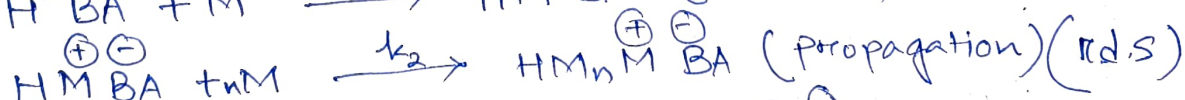
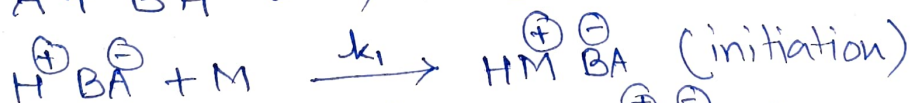
(I) Donation of a  $H^+$  to the counter anion.



(II) Formation of covalent bond between carbocation and counter anion.



### Kinetics of cationic chain polymerisation



$$\frac{d[M^+]}{dt} = k_1 [M][H^+]$$

$$-\frac{d[M]}{dt} = k_2 [M][M^+] \text{ (r.d.s)}$$

$$-\frac{d[M^+]}{dt} = k_3 [M^+]$$

Applying steady state approximation to  $M^+$

$$k_1 [M][H^+] = k_3 [M^+]$$

$$\Rightarrow [M^+] = \frac{k_1}{k_3} [M][H^+]$$

$$\therefore -\frac{d[M]}{dt} = \left(\frac{k_1 k_2}{k_3}\right) [M]^2 [H^+]$$

Kinetic chain length,

$$\gamma = \frac{\text{rate of propagation}}{\text{rate of initiation}}$$

$$= \frac{\left(\frac{k_1 k_2}{k_3}\right) [M]^2 [H^+]}{k_1 [M][H^+]}$$

$$= \frac{k_2}{k_3} [M]$$

$$\overline{D_p} = \gamma$$

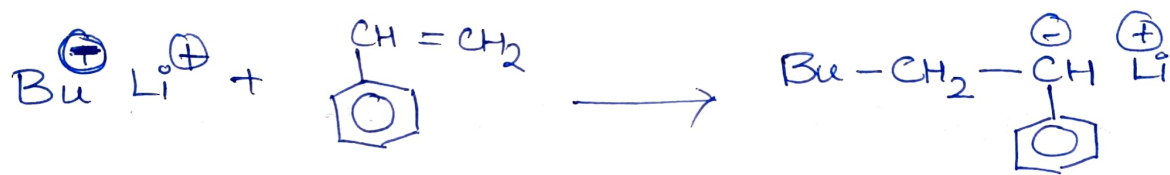
### Mechanism of Anionic Chain Polymerisation

\* Monomers with electron withdrawing substituents readily undergo anionic polymerisation. Eg. Nitrile, Carbonyl, ester etc.

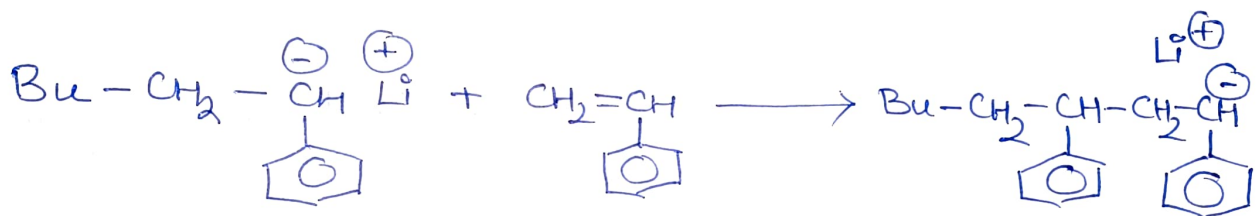
\* Initiators used  $\rightarrow$

- i. Grignard reagent
- ii. Alkali metals (Na & K) in liq.  $NH_3$
- iii. n-butyl lithium
- iv. Sodium complex of naphthalene

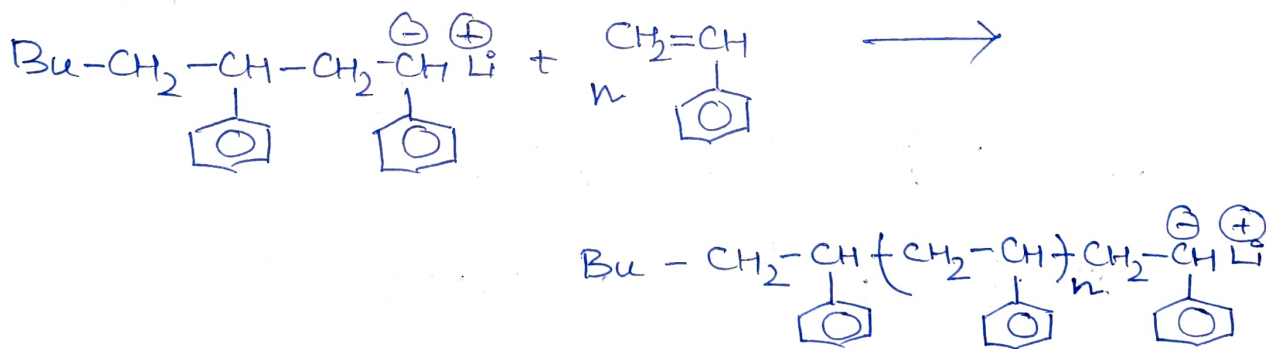
1. Initiation. The <sup>initiator</sup> anion attacks the monomer to form a carbanion.



2. Prepropagation. The carbanion then attacks another monomer and so on,



Prepropagation will proceed until all the monomers are consumed.

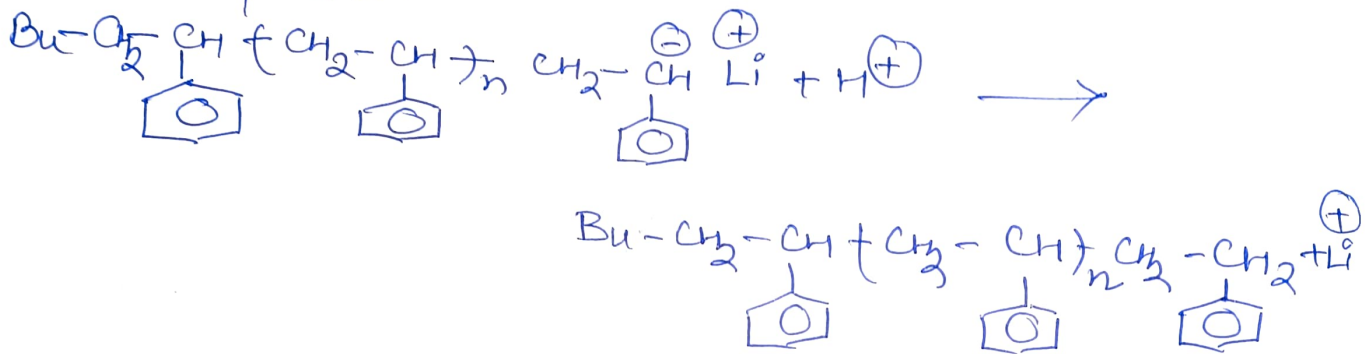


Living polymer: The termination of anionic polymerisation is not a spontaneous process.

If the polymerisation is carried out under controlled conditions and impurities are avoided, the reaction will proceed until all monomers are consumed and the carbanion remains potentially active.

If a fresh quantity of monomer is added the polymerisation again goes on until all the freshly added monomers are consumed.

3. Termination. Chain termination occurs upon addition of acid or a strongly ionic compound.



Kinetics of anionic chain polymerisation

Consider the following steps.



$$\frac{d[\text{M}^\ominus]}{dt} = k_1 [\text{M}] [\text{I}]$$

$$- \frac{d[\text{M}]}{dt} = k_2 [\text{M}^\ominus] [\text{M}] \quad (\text{r.d.s})$$

$$- \frac{d[\text{M}^\ominus]}{dt} = k_3 [\text{M}^\ominus] [\text{H}^+]$$



Applying steady state approximation to  $M^{\ominus}$

$$k_1 [M][I] = k_3 [M^{\ominus}][H^+]$$

$$\Rightarrow [M^{\ominus}] = \frac{k_1}{k_3} \frac{[M][I]}{[H^+]}$$

$$\therefore -\frac{d[M]}{dt} = \frac{k_1 k_2}{k_3} \frac{[M]^2 [I]}{[H^+]}$$

Kinetic chain length,

$$\bar{\gamma} = \frac{\left(\frac{k_1 k_2}{k_3}\right) \frac{[M]^2 [I]}{[H^+]}}{k_1 [M][I]}$$

$$= \frac{k_2}{k_3} \frac{[M]}{[H^+]}$$

$$\bar{D}_P = \bar{\gamma}$$

For a living polymer the following assumptions are considered

(i) The entire quantity of initiator dissociates at the same time.

(ii) All the anions formed initiate chain growth essentially simultaneously.

(iii) All the anions compete equally for the monomer.

$$\bar{D}_P = \frac{[M]}{[H^+]} \quad \text{for monoanion}$$

$$\bar{D}_P = \frac{2[M]}{[H^+]} \quad \text{for dianion.}$$