Ionic polymerization

The active center in this type of polymerization is positive or negative ions, known as carbonium or carbanion respectively.

The ionic polymerization differ from free radical polymerization by that:

1- The system of polymerization is heterogeneous because the initiators are always inorganic materials.

2- Very high rate of reaction and very high M.wt. polymer.

3- Presence of co catalyst beside the initiator or the catalyst. The co catalyst form ion pair as a counter ion with the growing ion. The propagation step is the insertion of the monomer between the ion pair to form a new active center.

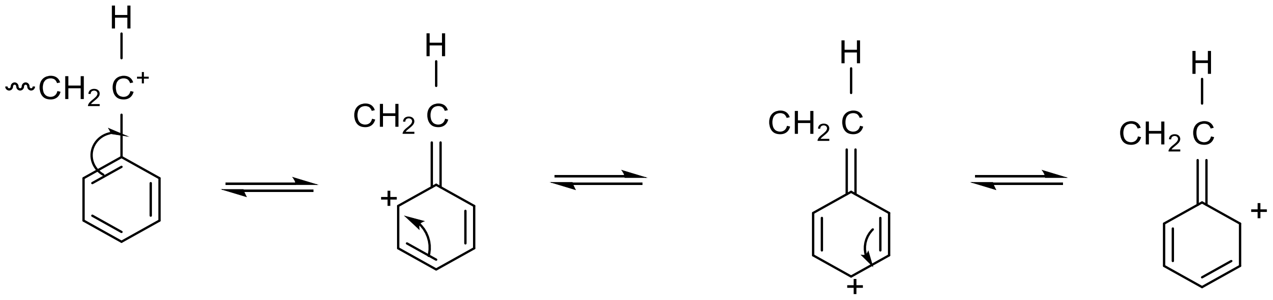
Cationic polymerization

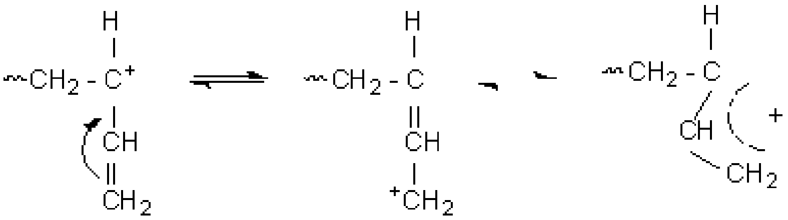
The active center in this type of polymerization most be positive ion. These positive centers may be on carbon atom or other atoms like nitrogen or oxygen or sulfur as below:

R_3C^+	H_3C^+	R_3S^+	R_3O^+
carbenium	**carbonium**	**sulfonium**	**oxonium**

$R\text{-}N \equiv N^+$	$R\text{-}O^+ \equiv CR_2$
dizonium	carboxonium

These positive ions are kinetically unstable. The presence of neighbor denoting group like OR, SR phenyl, or N_2R increase the stability of the ions through resonance (delocalization) or inductive effect.





Mechanism

Initiation step

There are many type of initiators can be used as below:

1) Organic salt that can supply stable carbenium ions: like CH_3CO^+ , ClO_4^- or $[(C_6H_5)_3C]^+[ClO_4]^-$ which can be dissociate in polar solvent to positive and negative ions

$$[(C_6H_5)_3C]^+[ClO_4]^- \rightarrow (C_6H_5)_3C^+ + ClO_4^-$$

To increase the rate of the process, some co catalyst was added (Gegen- ions)

$$[(C_6H_5)_3C]^+[ClO_4]^- + SbCl_5 \rightarrow [(C_6H_5)_3C^+SbCl_6^-$$

2) Lewis acids: like $AlCl_3$, BF_3, $SnCl_4$, $TiCl_4$

These catalyst must be ionized before attack with the monomers

$$2AlCl_3 \rightarrow AlCl_2^+ + AlCl_4^-$$

$$2BF_3 \rightarrow BF_2^+ + BF_4^-$$

These initiators are used to initiate the polymerization at low temperature and to get high M.wt. polymers.

Co catalyst must be used with this type of initiator like water, ether, or some alkyl halide. The co catalyst form complex with the initiator (ion pair)

$$BF_3 + H_2O \rightarrow H^+(BF_3OH)^-$$

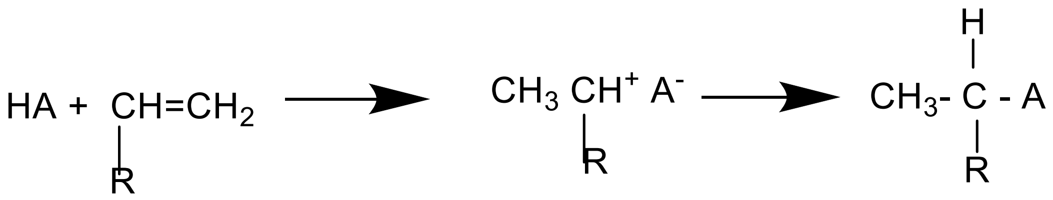
The proton was added to the monomer and the negative ion stay behind the new positive active center.

It was noticed that isobutylene did not polymerized in presence of dry BF_3, but polymerized directly in presence of some drops of water with BF_3.

3) protonic acids:

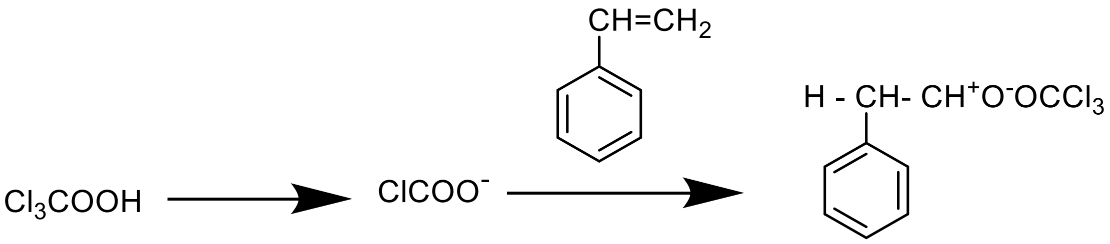
These acids give proton to the vinyl monomer and initiate the cationic polymerization when dissociate to proton and negative ions.

The acid must be strong acid and the negative ion must be weak nucleophile whereby if this negative ion is strong, it can bond with the positive growing center and terminate the reaction, so that halogenic acid did not used but other like sulfuric acid , phosphoric acid or perchloric acid are used.



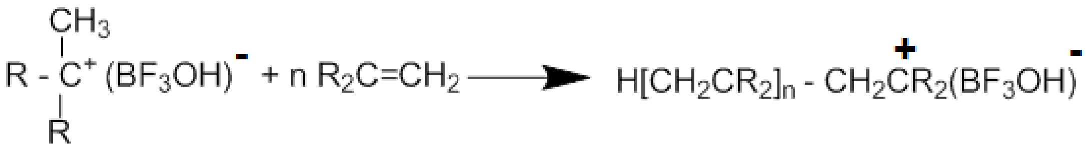
$$\mathrm{HA} + \underset{\mathrm{R}}{\mathrm{CH{=}CH_2}} \longrightarrow \mathrm{CH_3}\,\underset{\mathrm{R}}{\mathrm{CH^+}}\,\mathrm{A^-} \longrightarrow \mathrm{CH_3}-\overset{\mathrm{H}}{\underset{\mathrm{R}}{\mathrm{C}}}-\mathrm{A}$$

In using trichloro acetic acid for styrene polymerization, it was noticed that the yield and the M.wt. of the polystyrene is low when using small amount of the acid as initiator, But the yield and the M.wt. increased when using large amount of acid, this is because the trichloro acetate ion did not react with the positive active center of styrene chain, but neutralized with the excess amount of the acid.



Propagation step:

It was the insertion of the monomer molecule between the ion pair and added to the double bond to form new cation.



$$\mathrm{R}-\overset{\mathrm{CH_3}}{\underset{\mathrm{R}}{\mathrm{C^+}}}\,(\mathrm{BF_3OH})^- + n\,\mathrm{R_2C{=}CH_2} \longrightarrow \mathrm{H[CH_2CR_2]_n}-\mathrm{CH_2}\overset{+}{\mathrm{C}}\mathrm{R_2}(\mathrm{BF_3OH})^-$$

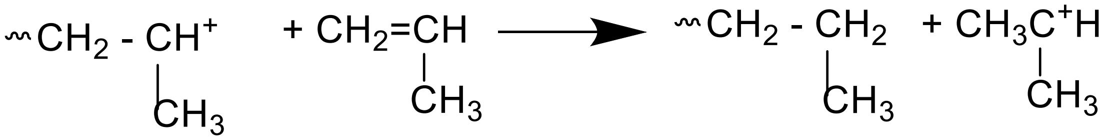
Termination step:

The types of termination reaction can be:

1) Spontaneous termination (elimination) by recombination between the two parts of catalyst and co catalyst

$$\mathbf{H[CH_2CR_2]_nCH_2CR_2^+(BF_3OH)^- \rightarrow H^+[BF_3OH]^- + H[CH_2CR_2]_nCH{=}CR_2}$$

2) Chain transfer to monomer



$$\sim CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH^+}} + \underset{\displaystyle CH_3}{\underset{|}{CH_2{=}CH}} \longrightarrow \sim CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH_2}} + \underset{\displaystyle CH_3}{\underset{|}{CH_3C^+H}}$$

3) By coupling between the two parts of the ion pair

$$\mathbf{H[CH_2CR_2]_nCH_2CR_2^+[BF_3OH]^- \rightarrow H[CH_2CR_2]_nCH_2CR_2OH + BF_3}$$

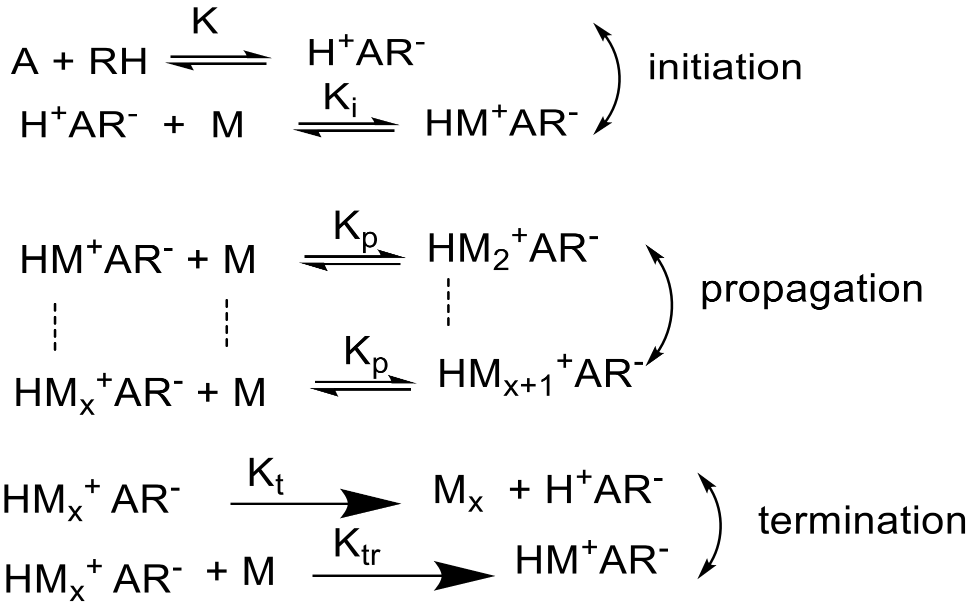
4) Transfer of hydride ion from monomer molecule to the polymer chain

$$\mathbf{H[CH_2CR_2]_nCH_2CR_2^+[BF_3OH]^- + CH_2{=}CR_2 \rightarrow H[CH_2CR_2]_nCH_2CHR_2 + CH_2CR^+\{BF_3OH)^-}$$

Kinetics:

A is the catalyst / RH is the co catalyst / M is the monomer

The cationic polymerization steps are:



$$\left.\begin{array}{l} A + RH \underset{}{\overset{K}{\rightleftharpoons}} H^+AR^- \\ H^+AR^- + M \overset{K_i}{\rightleftharpoons} HM^+AR^- \end{array}\right\} \text{initiation}$$

$$\left.\begin{array}{l} HM^+AR^- + M \overset{K_p}{\rightleftharpoons} HM_2^+AR^- \\ \quad\vdots \\ HM_x^+AR^- + M \overset{K_p}{\rightleftharpoons} HM_{x+1}^+AR^- \end{array}\right\} \text{propagation}$$

$$\left.\begin{array}{l} HM_x^+AR^- \xrightarrow{K_t} M_x + H^+AR^- \\ HM_x^+AR^- + M \xrightarrow{K_{tr}} HM^+AR^- \end{array}\right\} \text{termination}$$

Rate of polymerization $v_p = \frac{-d[M]}{dt}$

$$= K_p\,[M][M^+] \ldots\ldots\ldots\ldots 1$$

Rate of initiation $v_i = \frac{d[M^+]}{dt}$

$$= KK_i[A][RH][M] \;\ldots\ldots\ldots\ldots 2$$

Rate of termination $v_t = -\frac{d[M^+]}{dt} = K_t[M^+] \;\ldots\ldots\ldots\; 3$

At the steady state $v_i = v_t$

From 2 and 3

$$[M^+] = \frac{KK_i}{K_t}[A][RH][M] \;\ldots\ldots\ldots\; 4$$

Substituting 4 in 1

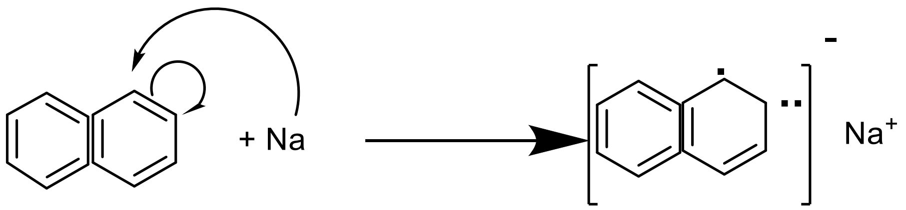
$$\text{rate of polymerization} = \frac{K_iK_p}{K_t}K[A][RH][M]^2 \;\ldots\ldots\ldots\ldots\; 5$$

$$\textbf{degree of polymerization } \overline{\mathbf{Dp}} = \frac{\mathbf{Rp}}{\mathbf{Rt}} = \frac{K_p}{K_t}[M] \;\ldots\ldots\; 6$$

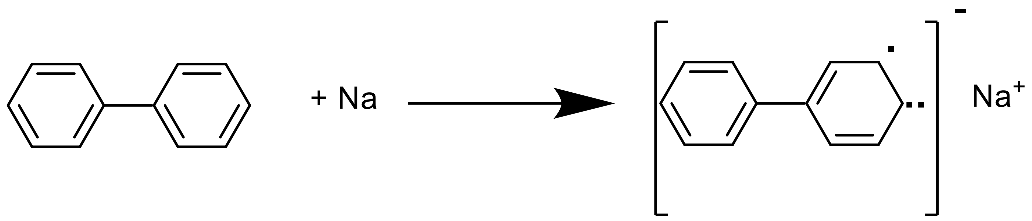
Anionic polymerization

The active center in this type of polymerization is the anion. The suitable monomers must contain electron withdrawing groups. This groups decrease the density of charge by resonance or induction effect. There are many types of withdrawing groups like nitrile (CN), carbonyl (C=0). The three steps of polymerization reaction are initiation, propagation and termination. The used **initiators** are of many types:

a) Alkali metals, like sodium which start the reaction by transfer the electron from the metal to the monomer. Before this step there is the co-catalyst like naphthalene, anthracene or biphenyl, whereby the electron transfer to their from the metal to form aromatic free radical anion.

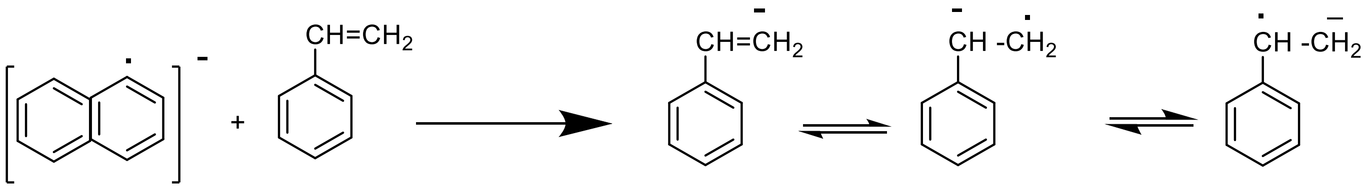


sodium naphthalene



sodium biphenyl

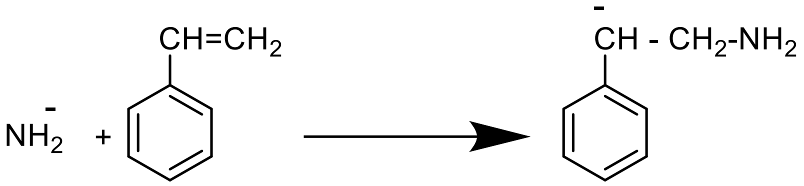
The electron transfer from the free radical anion to the monomer.



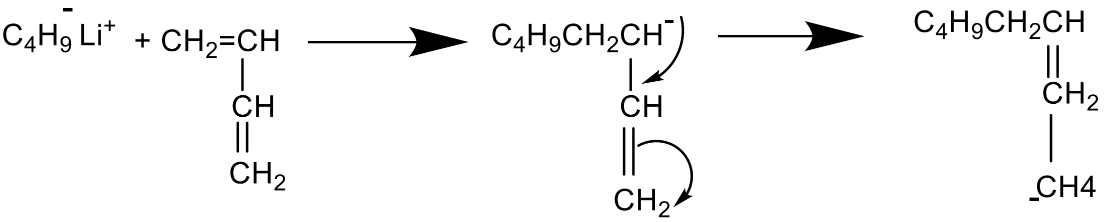
Or by using the alkali metal in ammonia to form amide ion $\overset{-}{NH_2}$

$$K + NH_3 \rightarrow KNH_2 + H^+$$

The amide ion attack the monomer

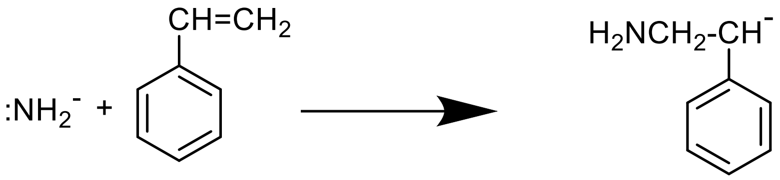


b) Metal alkyls, like Butyl lithium or triphenyl methyl sodium



c) Metal amide, like sodium amide or potassium amide

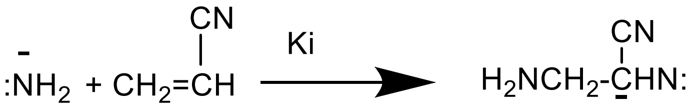
$$KNH_2 \rightleftharpoons K^+ + :NH_2^-$$



Reaction mechanism and kinetics:

Take acrylonitrile as an example

- Initiation step

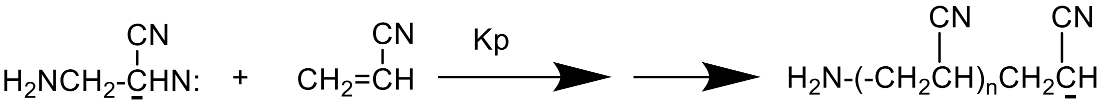


$$\overset{-}{:NH_2} + CH_2{=}\overset{CN}{\overset{|}{C}}H \xrightarrow{Ki} H_2NCH_2\text{-}\underset{-}{\overset{CN}{\overset{|}{C}}}HN: \text{ -------------- } 1$$

$Ri = Ki[C][M]$

$C = :\overset{-}{N}H_2$

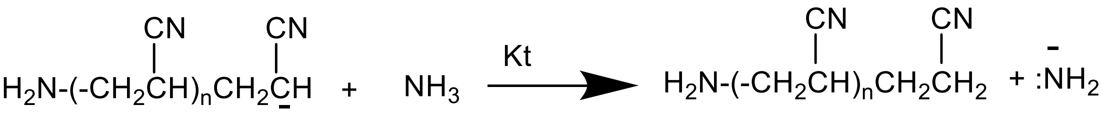
- Propagation step:



$$H_2NCH_2\text{-}\underset{-}{\overset{CN}{\overset{|}{C}}}HN: + CH_2{=}\overset{CN}{\overset{|}{C}}H \xrightarrow{Kp} \longrightarrow H_2N\text{-}(\text{-}CH_2\overset{CN}{\overset{|}{C}}H)_nCH_2\underset{-}{\overset{CN}{\overset{|}{C}}}H$$

$Rp = Kp[M][M^-]$ ----------- 2

- Termination step: occurred through solvent transfer



$$H_2N\text{-}(\text{-}CH_2\overset{CN}{\overset{|}{C}}H)_nCH_2\underset{-}{\overset{CN}{\overset{|}{C}}}H + NH_3 \xrightarrow{Kt} H_2N\text{-}(\text{-}CH_2\overset{CN}{\overset{|}{C}}H)_nCH_2\overset{CN}{\overset{|}{C}}H_2 + :\overset{-}{N}H_2$$

$Rt = Kt[NH_3][M^-]$ ----------- 3

At steady state Ri =Rt

$$[M^-] = \frac{Ki[C][M]}{Kt[NH3]}$$

Substitution in equation 2

$$Rp=\frac{Kp[M]Ki[C][M]}{Kt[NH_3]}=\frac{K^{/}[M]^2[C]}{[NH_3]}$$

Degree of polymerization

$$\overline{Dp}=\frac{Rp}{Rt}=\frac{Kp[M][M^-]}{Kt[NH_3][M^-]}=\frac{k^{\backslash}[M]}{[NH_3]}$$

Living polymers:

The absence of the termination step in anionic polymerizations with carefully purified reactants in inert reactions media results a living polymers. Whereby termination is not found. In such systems, the growing species remain dormant in the absence of monomers but resume their growth activity with a fresh monomer supply.

With adequate mixing, the monomer supplied to the system is distributed among the growing centers (living polymers). As a result, the number-average degree of polymerization is simply the ratio of the number of moles of monomer added to the total number of living polymers. That is

$Dp= [M]/[C]$

Living polymers are generally characterized by:

(1) An initiation rate is very much larger than the polymerization rate.

(2) Linear molecular weight conversion relationship

(3) Narrow molecular distribution.

4) Linear and stereo regular polymers.

(5) Stabilization of the living end groups allowing the formation of macromers, block copolymers and star polymers.