Kinetics of Polymerisation

Dr. Subhra Mishra

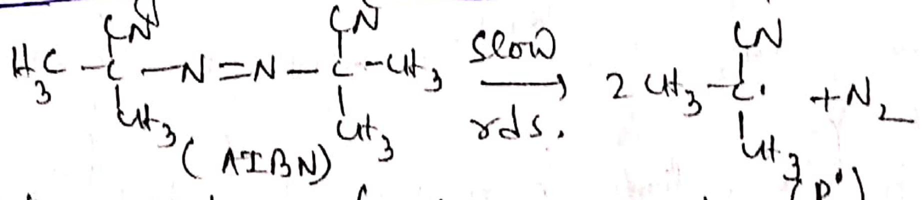
Process of Polymerisation: Polymerisation is possible only if ΔG is -ve for the transformation of monomer to polymer. This will depend only upon the initial and final states, not the nature of the intermediate (free radical, anion, cation etc) High polymer is formed immediately in a chain reaction. Increasing the reaction time simply increases the amount of high polymer produced.

The process of combination of the constituent monomers is polymerisation and it can occur through three ways —
(i) addition polymerisation
(ii) condensation polymerisation
& (iii) ring opening polymerisation

~~Theeeeree~~ They can occur through free radical and ionic (cationic & anionic) mechanism. Almost all substituents allow resonance delocalisation. Electron-withdrawing substituents lead to anionic mechanism. Electron-donating substituents lead to cationic mechanism. Polymerisation kinetics tell us how fast the system takes various reaction paths.

Addition polymerisation: It can undergo through both free radical & ~~o~~ ionic mechanism.

(i) Free radical mechanism- It occurs in three steps initiation, propagation and termination. To initiate the process, some free radical producers are to be added. The organic peroxides are the common free radical producers. Azobisisobutyronitrile (AIBN) is also a free radical producer.



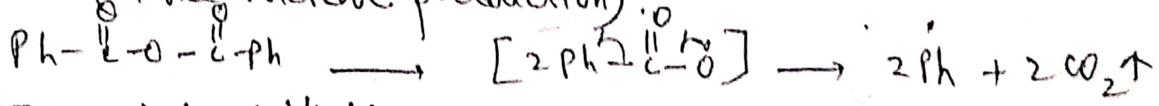
$$H_3C-\underset{CH_3}{\overset{CN}{C}}-N=N-\underset{CH_3}{\overset{CN}{C}}-CH_3 \xrightarrow[rds.]{slow} 2\,CH_3-\underset{CH_3}{\overset{CN}{\dot{C}}} + N_2$$

(AIBN) (R$^\cdot$)

(Initiator) $I \xrightarrow{k_d} 2\dot{R}$

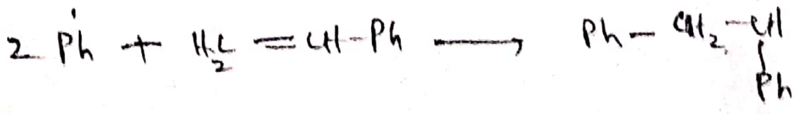
For polymerisation of styrene in presence of benzoyl peroxide (free radical producer), the steps are given below—

Step 1: (Free radical production):



$$Ph-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-Ph \longrightarrow [2Ph-\overset{O}{\overset{\|}{C}}-\dot{O}] \longrightarrow 2\dot{Ph} + 2CO_2\uparrow$$

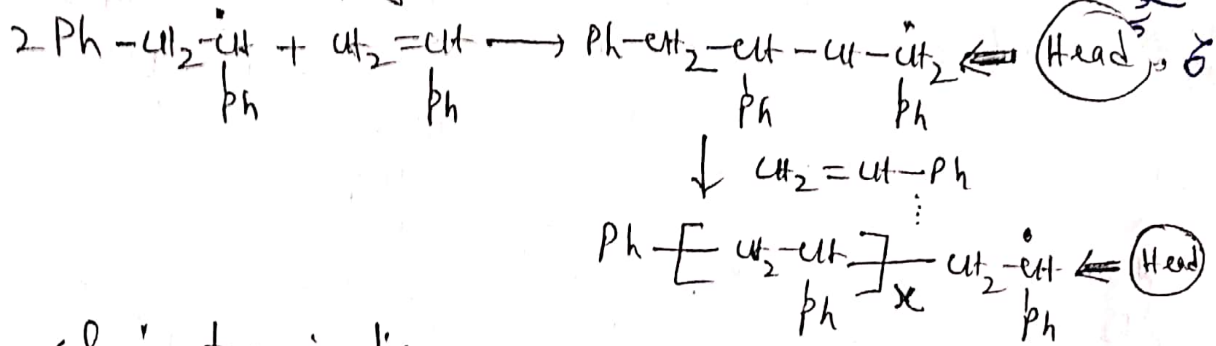
Step II: chain initiation



$$2\dot{Ph} + H_2C=CH-Ph \longrightarrow Ph-CH_2-\underset{Ph}{\dot{C}H}$$

$\leftarrow$ Lead

Step III: Chain propagation

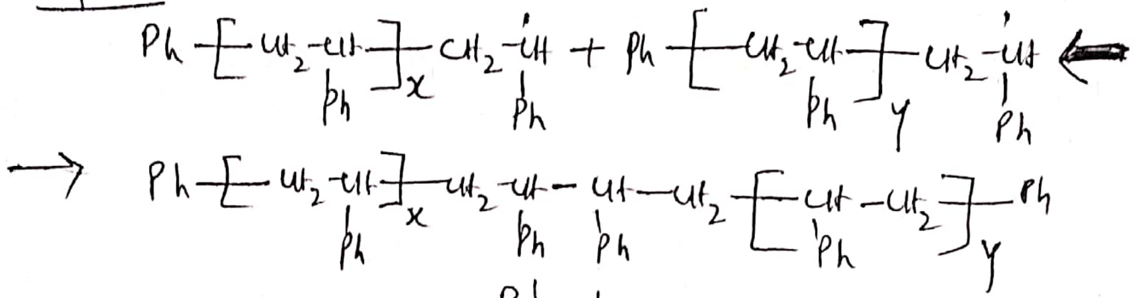


$$2\,Ph-CH_2-\underset{Ph}{\dot{C}H} + \underset{Ph}{CH_2=CH} \longrightarrow Ph-CH_2-\underset{Ph}{CH}-CH-\underset{Ph}{\dot{C}H_2} \Leftarrow \text{Head}$$

$$\downarrow CH_2=CH-Ph$$

$$Ph-\left[CH_2-\underset{Ph}{CH}\right]_x-CH_2-\underset{Ph}{\dot{C}H} \Leftarrow \text{Head}$$

Step-IV Chain termination



$$Ph-\left[CH_2-\underset{Ph}{CH}\right]_x-CH_2-\underset{Ph}{\dot{C}H} + Ph-\left[CH_2-\underset{Ph}{CH}\right]_y-CH_2-\underset{Ph}{\dot{C}H}$$

$$\longrightarrow Ph-\left[CH_2-\underset{Ph}{CH}\right]_x-CH_2-\underset{Ph}{CH}-\underset{Ph}{CH}-CH_2-\left[\underset{Ph}{CH}-CH_2\right]_y-Ph$$

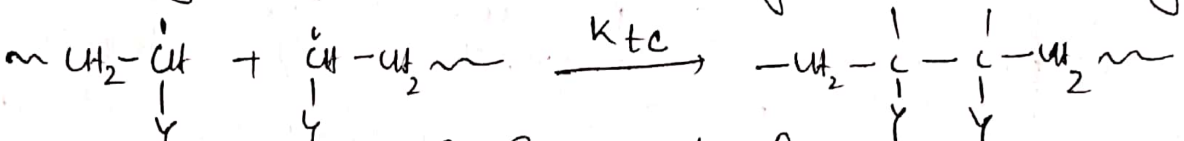
Always the same identity and reactivity for head to tail

Poly styrene

$CH_2=CH-X$ ($X = Cl, CN, -OH, H$) can undergo polymerisation through free radical mechanism.

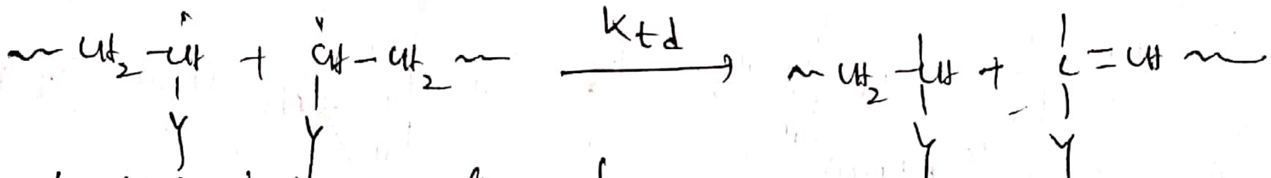
Termination reactions are similar for radical and cationic. They occur through any one of coupling and ~~disproportion~~ disproportionation steps.

Coupling (where molecular weight is effectively doubled)



$$\sim CH_2-\underset{Y}{\dot{C}H} + \underset{Y}{\dot{C}H}-CH_2\sim \xrightarrow{K_{tc}} -CH_2-\underset{Y}{C}-\underset{Y}{C}-CH_2\sim$$

Disproportionation (where molecular weight is unchanged)



$$\sim CH_2-\underset{Y}{\dot{C}H} + \underset{Y}{\dot{C}H}-CH_2\sim \xrightarrow{K_{td}} \sim CH_2-\underset{Y}{CH} + \underset{Y}{C}=CH\sim$$

Most anionic reactions have no inherent termination step.

Head ②

~~Kinetics of free radical polymerisation~~. Rate of reaction of polymerization is proportional to the concentration of ~~[illegible]~~ or disappearance of monomer in a particular reaction.

Rate of reaction = Constant x $[\text{Concentration}]^n$ terms.

or

Rate of disappearance of monomer $= -\frac{dM}{dt}$

$= K\,[\text{concentration}]^n$ terms.

Kinetics of free radical polymerization: The overall mechanism for the conversion of a monomer to a polymer via free radical initiation may be described using steady state Kinetics approaches –

(i) Initiation: This is a two step process involving

A. decomposition of the initiator into primary radicals

$$I_2 \xrightarrow{K_d} 2R^\cdot \text{;}$$ K_d = Rate constant for initiator decomposition

B. The addition of a monomer to the primary free radical

$$R^\cdot + M \xrightarrow{K_a} RM^\cdot_i$$ where, K_a is the rate constant for monomer addition.

Since Initiator decomposition is much slower than monomer addition, the first step of the initiation step ~~(K_d)~~ ($K_a \gg K_d$) is the rate limiting step. Some of the initiator radicals may ~~be~~ undergo side reactions (secondary) such as combination with another radical etc. Therefore, only a fraction, f (an efficiency factor), of the initial initiator molecule produces a pair of free radicals, either one or both of which can initiate polymerization.

So, the rate expression for initiation may be written as – ~~$-\frac{d[M^\cdot]}{dt}$~~

$$R_i \; -\frac{d[I]}{dt} = \frac{1}{2}\frac{d[M^\cdot]}{dt} = K_d[I]$$

As only a fraction f radicals initiate chain growth

Therefore, $R_i = \frac{d[M^\cdot]}{dt} = 2fK_d[I]$

(ii) Propagation: The successive addition of monomers propagation may be represented as follows —

$$RM_1^\cdot + M \xrightarrow{k_p} RM_2^\cdot$$

$$RM_2^\cdot + M \xrightarrow{k_p} RM_3^\cdot$$

In general, $RM_x^\cdot + M \xrightarrow{k_p} RM_{x+1}^{\Sigma}$

In this case, it is assumed that radical reactivity is independent ~~of~~ of chain length, which means all propagation steps have the same rate constants k_p. Propagation is a fast process. eg. under typical condition, a polymer of molecular wt of about 10^7 may be produced in 0.1 s. It may therefore be assumed that number of monomer molecule reacting in the second initiation step is insignificant compared with the consumed in the propagation step. Thus the rate of polymerization equals essentially the rate of consumption of ~~for~~ monomer in the propagation step. Therefore, the rate for polymerization can be expressed as —

$$R_p = -\frac{d[M]}{dt} = k_p[M^*][M]$$

where, $[M^*] = \Sigma RM_x^\cdot$ ie the sum of the concentrations of all chain radicals of type RM_x.

(iii) Termination: Chain growth may be terminated at any point during polymerisation by using following one or two mechanistic pathways —

- Combination (coupling)

$M_x^\cdot + M_y^\cdot \xrightarrow{k_{tc}} M_{x+y}$; where K_{tc} = rate constant for termination process (combination)

- Disproportionation: $M_x^\cdot + M_y^\cdot \xrightarrow{k_{td}} M_x + M_y$ where k_{td} rate const for disproportion

If above both steps are kinetically equivalent, then termination may be represented as —

$M_x^\cdot + M_y^\cdot \xrightarrow{k_t} P$; where k_t is the rate constant for overall termination reaction.

the termination rate may be given as —

$$R_t = \frac{-d[M^\cdot]}{dt} = 2k_t[M^\cdot]^2$$

The factor of '2' arises from the fact that at each incidence of termination reaction, two radical disappear.

At steady state polymerization, the total radical concentration remains constant, which means that radicals are being produced and destroyed at equal rates (ie, $R_i = R_t$)

so, $$[M^\cdot] = \left(\frac{fk_d}{k_t}\right)^{1/2}[I]^{1/2}$$

[By combining rate ~~eq~~ equation of initiation with termination]

Since, The overall polymerisation rate is essentially the rate of monomer consumption during propagation, substitution the the previous expression ($M^\cdot$) in the rate eqn of propagation, the final equation may be like —

$$R_p = k_p\left(\frac{fk_d}{k_t}\right)^{\frac{1}{2}}[I]^{\frac{1}{2}}[M]$$

According to the ~~rate~~ equation, the rate of polymer formation in free radical polymerisation is first order in monomer concentration and half order in initiator concentration.

This assumes that the initiator ~~e~~ efficiency is independent of monomer concentration and half order in initiator concentration. Sometimes Kinetic study indicates ~~that~~ a decrease in f with dilution, although the decrease have been invariably small.

Problem 1: The following ~~rate~~ are data for the polymerization of styrene in benzene at 60°C with benzoyl peroxide as the initiator.

$[M] = 3.34 \times 10^3$ mol/m^3, $[I] = 4.0$ mol/m^3

$k_p^2/k_t = 0.95 \times 10^{-6}$ m^3/mol^{-1} s^{-1}, calculate the initial rate of polymerization.

Solution: Assuming the initiator efficiency $f = 1$, then rate of Polymerization, $R_p = k_p(k_d/k_t)^{1/2}[I]^{\frac{1}{2}}[M]$

$$R_p^2 = k_d(k_p^2/k_t)[I][M]^2$$

⑥

$$= \left(3.2 \times 10^{-6} \frac{m^3}{mol.s}\right)\left(0.95 \times 10^{-6} \frac{m^3}{mol.s}\right)\left[4.0 \frac{mol}{m^3}\left(3.34 \times 10^{3} \frac{mol}{m^3}\right)\right]^{2}$$

$$R_p = 11.65 \times 10^{-3} \ mol/m^3\text{-}s.$$

$$R_p = 0.012 \ mol/m^3\text{-}s.$$

Kinetic chain length: the kinetic chain length, ν, is defined as the average number of monomers consumed by each primary radical. so, the magnitude of the kinetic length will depend on the rate of the propagation relative to the termination rate ie.

$$\nu = \frac{R_p}{R_t}$$

Since at steady state the rate of initiation equals the rate of termination, so,

$$\nu = \frac{R_p}{R_t} = \frac{R_p}{R_i}$$

Putting the value of R_p, R_i from the earlier equation -

$$\nu = \frac{k_p}{2\left(f k_d k_t\right)^{\frac{1}{2}}} \cdot \frac{[M]}{[I]^{1/2}}$$