

* Also $X(M) = \sum_0^M x_m = \int_0^M X_m dM$

* Weight Fraction $W_m = \frac{N_m M}{\sum N_m M}$ and $W(M) = \sum_0^M W_m = \int_0^M W_m dM$

* Normalised Moments; $\overline{M}_j = \frac{\sum N_m M^j}{\sum N_m M^{j-1}}$ & $\overline{DP}_j = \frac{\sum N_r r^j}{\sum N_r r^{j-1}}$

so 1st moment = number averages

2nd moment = weight averages

Note: $\frac{\overline{M}_w}{\overline{M}_n} = \text{polydispersity index}$

\overline{M}_w ← 2nd moment
 \overline{M}_n ← 1st moment

* Continuous functions to describe MMDs;

① Most probable; $W_m = \frac{M}{M_w^2} \exp\left(-\frac{M}{M_w}\right)$

② Log normal; suitable for addition polymerisation

Stepwise (Condensation) Polymerisation

* A "poly-functional" molecule can react at 2 or more sites, combines with another resulting in a polymer and a small molecule (e.g. H₂O) being released.

* For a monomolecular system $p(\text{extent of reaction}) = \frac{N_0 - N}{N_0}$

N_0 ← number of reacted groups.
 N_0 ← number of molecules at $t=0$

$$\Rightarrow \overline{DP}_n = \frac{\sum N_r r}{\sum N_r} = \frac{N_0}{N} = \frac{1}{1-p}$$

$$\Rightarrow \overline{M}_n = \frac{M_0}{1-p}$$

← more molecules react, their total number falls and their length becomes larger.

$\frac{dM}{dt} = \dots$ $\frac{dM}{dt} = (\text{initial value}) \dots$

Addition Polymerization Initiation \rightarrow Propagation \rightarrow Termination

Initiation

- (i) Thermal; Require high temps. e.g. $\text{CH}_2 = \text{CHX} \Rightarrow \text{CH}_3 - \text{CHX}^\bullet$
- (ii) VV; Typical for azo compounds and is easily controlled.
e.g. $(\text{CH}_3)_2\text{C}(\text{CN}) - \text{N} \equiv \text{N} - \text{C}(\text{CN})_2 - (\text{CH}_3)_2 \xrightarrow{\text{UV}} 2 \times \left[(\text{CH}_3)_2\text{C}(\text{CN})^\bullet \right] + \text{N}_2$
- (iii) Redox Reaction; e.g. $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \Rightarrow \text{Fe}^{3+} + \text{OH}^\bullet + \text{OH}^-$

Propagation



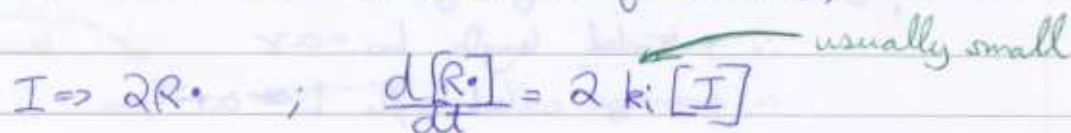
Often there is more than one possible reaction. The relative amount of each product depends on their activation energies.

Termination

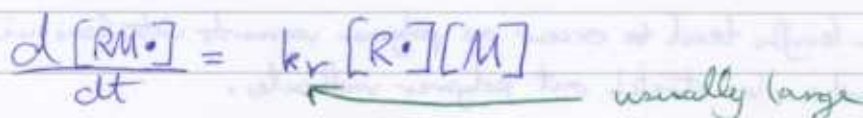
- (i) Combination; $\text{R}^\bullet + \text{R}^\bullet \Rightarrow \text{M}$ i.e. two radicals join together
- (ii) Disproportionation; An H atom is transferred between two radicals, forming one saturated and one unsaturated polymer chain.
- (iii) Reaction with Initiator; Occurs when initiator concentration is high.

Kinetics

* Assume initiator breaks down into two free radicals;



* Next an active site forms; $\text{R}^\bullet + \text{M} \Rightarrow \text{RM}^\bullet$;



For propagation; $\frac{d[P_r \cdot]}{dt} = k_p[M][P_r \cdot] - k_p[M][P_r \cdot]$

$$\therefore -\frac{d[M]}{dt} = k_p[M]([P_1 \cdot] + [P_2 \cdot] + \dots)$$

$$\Rightarrow -\frac{d[M]}{dt} = k_p[M] \sum [P_r \cdot] \leftarrow \text{consumption of monomer}$$

For termination; $-\frac{d[\sum P_r \cdot]}{dt} = 2k_t(\sum [P_r \cdot])^2$

* To solve consider steady state;

$$-\frac{d[\sum P_r \cdot]}{dt} = \frac{d[R \cdot]}{dt}$$

$$\Rightarrow 2k_t(\sum [P_r \cdot])^2 = 2k_i[I]$$

$$\Rightarrow \sum [P_r \cdot] = \sqrt{\frac{k_i[I]}{k_t}}$$

$$\therefore -\frac{d[M]}{dt} = \frac{k_p k_i^{0.5}}{k_t^{0.5}} [M][I]^{0.5}$$

Note $\bar{V} = \frac{\text{rate of addition of monomers to polymer chains}}{\text{rate of formation of polymer chains}}$

$$\therefore \bar{V} = \frac{-\frac{d[M]}{dt}}{\frac{d[R \cdot]}{dt}}$$

Polymer Chain Configuration

Chain length \rightarrow "r" links of length "a"

$$\therefore \text{extended length } L_0 = ar$$

$$\therefore \text{average coiled length } L \approx ar^{0.5}$$

\swarrow assuming no fixed bond angles

Assuming fixed bond angles; $L \approx ar^{0.5} \times \left(\frac{1 - \cos \theta}{1 + \cos \theta} \right)$

* Longer lengths tend to occur as polymer segments interfere with each other.

* Solvents also stretch out polymer molecules.