Condensation OR Step-growth polymerisation

* Polymer formation proceeds through a reaction between functional groups in a slow and step-wise manner.

* The active monomeres should have two $\overset{Reactive}{\underset{\wedge}{functional}}$ groups.

* Two types of functional groups are involved in the process, such as: Carboxylic acid / alcohol, Carboxylic acid / amine, alcohol / aldehyde etc.

* In some cases the monomere may contain both the types of reactive functional groups. (bifunctional monomere). Those are described as A-B type poly condensation.

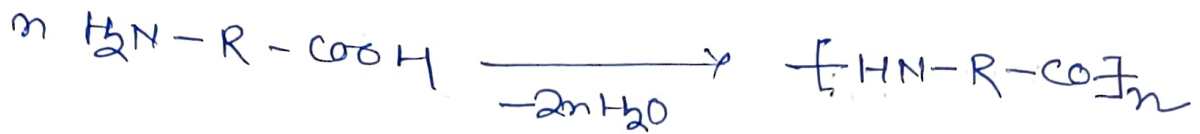$$m A-B \longrightarrow B \xleftarrow{} AB \xrightarrow{}_{n-1} A$$

* In other cases the bifunctional monomere may have same functional groups at both the ends. Eg → dialdehyde, diol etc. In this case two types of monomers are involved (A-A and B-B). and is called AA-BB type Condensation.
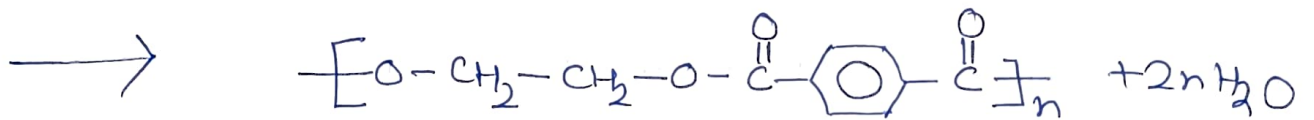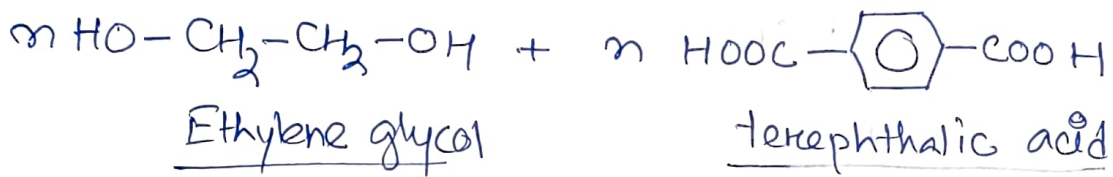
* At the end of the reaction both the functional groups are still present in the polymer → active or living polymer.

Examples

① Condensation of amino acids

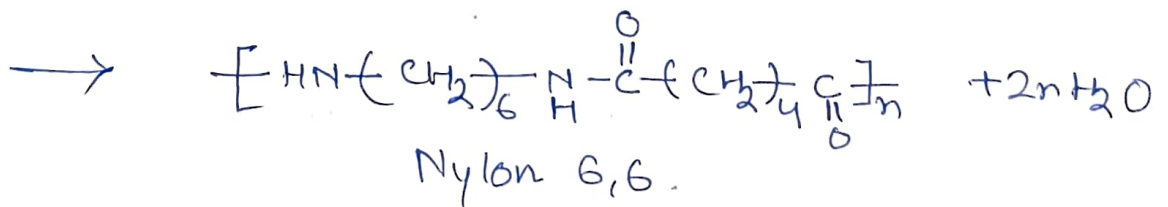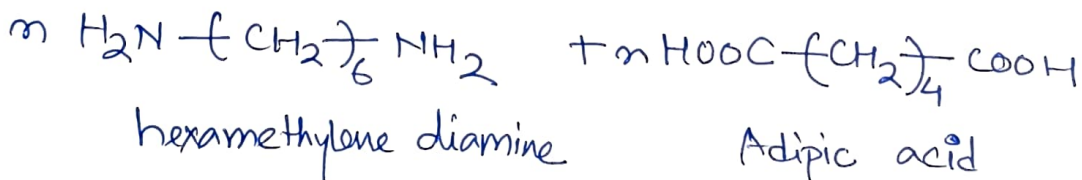$$n \; H_2N-R-COOH \xrightarrow{-2nH_2O} \{HN-R-CO\}_n$$

② Polyesters (PET: polyethylene terephthalate)

$$n \; HO-CH_2-CH_2-OH + n \; HOOC-\bigcirc-COOH$$

Ethylene glycol   terephthalic acid

$$\longrightarrow \; \{O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-\bigcirc-\overset{O}{\overset{\|}{C}}\}_n \; +2nH_2O$$

PET   or   Dacron   or   Terylene.

③ Polyamide (Nylon 6,6)

$$n \; H_2N\{CH_2\}_6 NH_2 + n \; HOOC\{CH_2\}_4 COOH$$

hexamethylene diamine   Adipic acid

$$\longrightarrow \; \{HN\{CH_2\}_6 \overset{}{\underset{H}{N}}-\overset{O}{\overset{\|}{C}}\{CH_2\}_4 \overset{}{\underset{O}{\overset{\|}{C}}}\}_n \; +2nH_2O$$

Nylon 6,6.

(IV) Phenol formaldehyde resin

$$\text{OH-}\bigcirc + HCHO \xrightarrow{Acid}$$

Novolac.

(v) Epoxy Resins :

$$n \; Cl-CH_2-CH-CH_2 \;\; + n \; HO-\langle ph \rangle-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\langle ph \rangle-OH$$

Epichlorohydrin   Bisphenol A

$$\longrightarrow \quad \Big[O-\langle ph \rangle-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\langle ph \rangle-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2 \Big]_n$$

$$+ n \; HCl$$

(vi) Polycarbonates

$$n \; HO-\langle ph \rangle-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\langle ph \rangle-OH \;\; + \; n \; Cl-\overset{\overset{O}{||}}{C}-Cl$$

Phosgene

$$\longrightarrow \quad \Big[O-\langle ph \rangle-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\langle ph \rangle-O-\overset{\overset{O}{||}}{C} \Big]_n \;\; + 2n \; HCl$$

Polycarbonate

(vii) Polyurethane

$$m \; HO-R-OH \;\; + \; n \; OCN-R'-NCO \;\; \longrightarrow$$

$$\Big[O-R-O-\overset{\overset{O}{||}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}-R'-\underset{\underset{||}{}}{\overset{\overset{H}{|}}{N}}-\overset{\overset{}{}}{\underset{\underset{O}{||}}{C}} \Big]_n$$
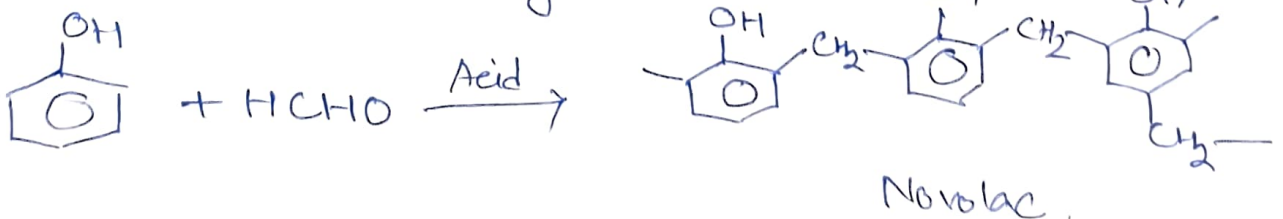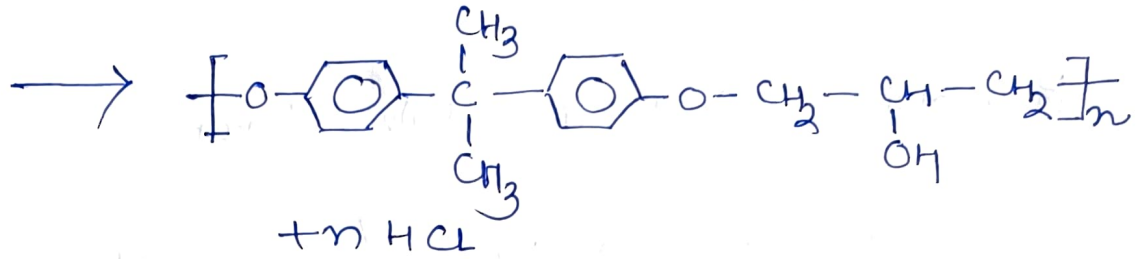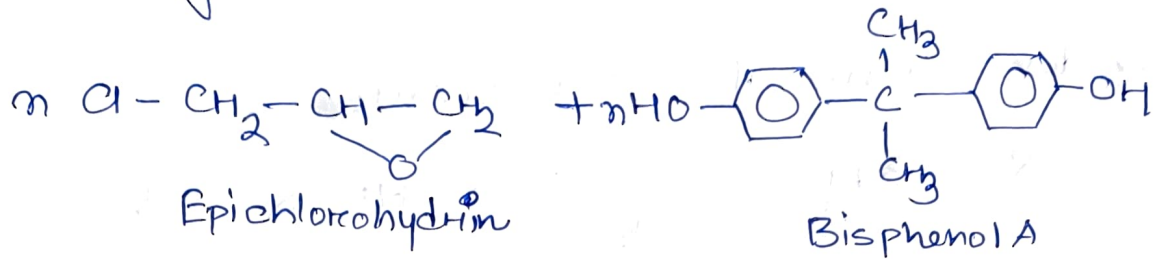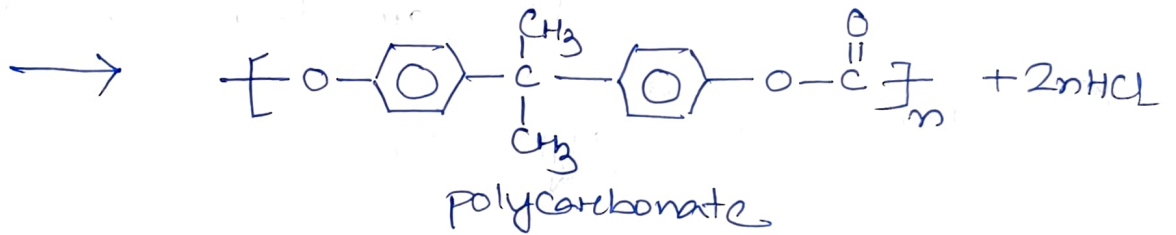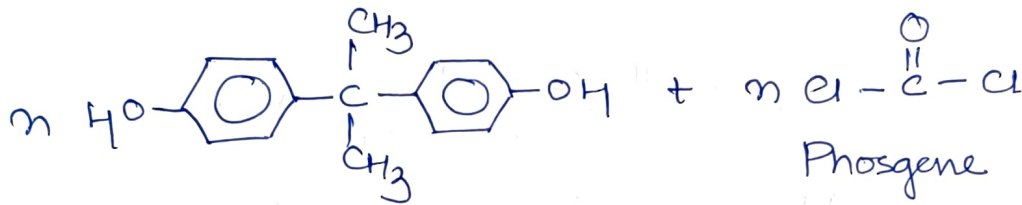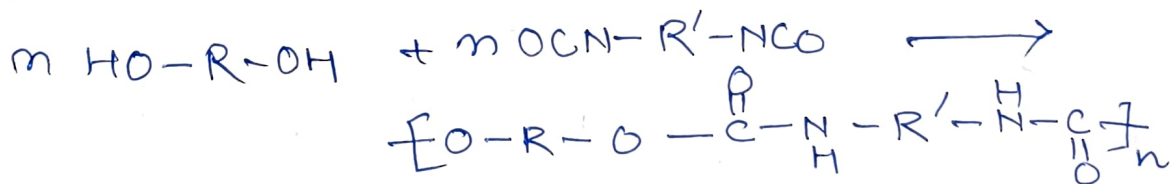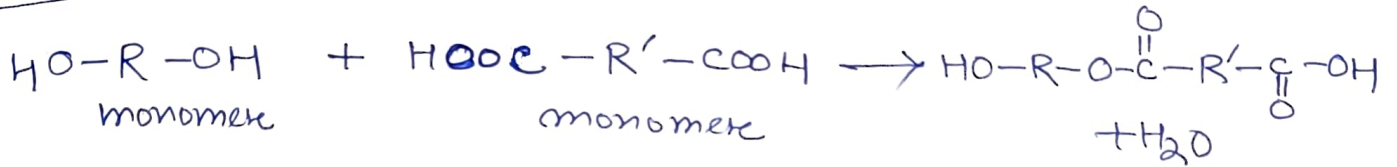
Mechanism

* Functionality : Number of reactive site in a monomere
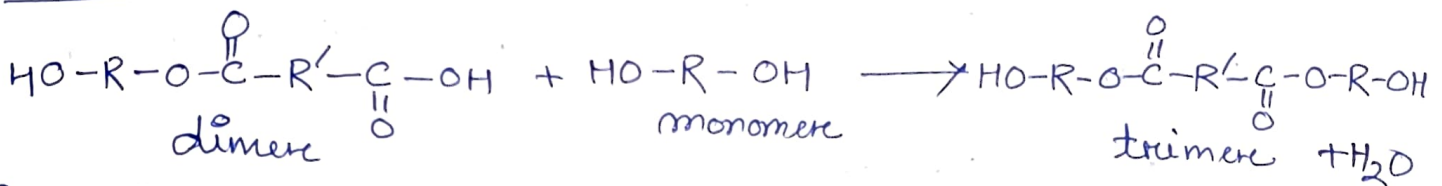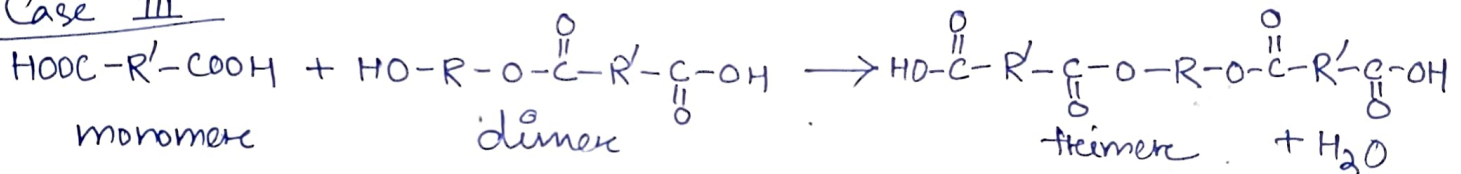
Case I

$$HO-R-OH + HOOC-R'-COOH \longrightarrow HO-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{C}}-OH$$

monomere   monomere $+H_2O$

Case II

$$HO-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{\underset{O}{C}}}-OH + HO-R-OH \longrightarrow HO-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{\underset{O}{C}}}-O-R-OH$$

dimere   monomere   trimere $+H_2O$

Case III

$$HOOC-R'-COOH + HO-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{\underset{O}{C}}}-OH \longrightarrow HO-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{C}}-O-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{C}}-OH$$

monomere   dimere   trimere $+H_2O$

Case IV

$$HO-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{\underset{O}{C}}}-OH + HO-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{C}}-OH$$

dimere   dimere

$$\longrightarrow HO-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{\underset{O}{C}}}-O-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{}{\underset{\|}{C}}-OH$$

tetramere $+H_2O$
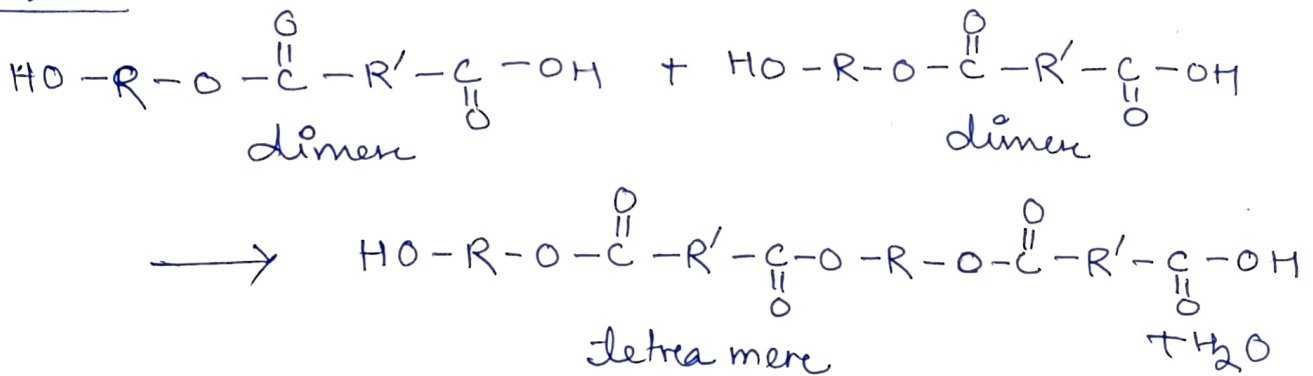
monomere + monomere → dimere

dimere + monomere → trimere

trimere + monomere → tetramere

tetramere + tetramere → octamere

m-mere + m-mere → $(m+m)$-mere

Flory's equal reactivity Principle

At any given time, mixture of a poly condensation reaction contains bifunctional 'mers'. The reactivity of both the functionalitys are same irrespective of their size.

Extent of reaction

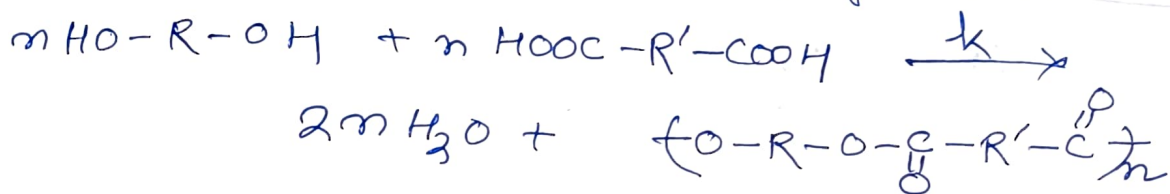fraction of functional groups that has reacted at Time, t

$$P = \frac{N_0 - N}{N_0}$$

N_0 = number of molecules present initially

N = number of molecules present at time, t

Types of Condensation reaction

(i) Self Catalysed polycondensation reaction

(ii) Acid catalysed poly Condensation reaction

Kinetics of self catalysed polycondensation

$$n \, HO-R-OH \; + \; n \, HOOC-R'-COOH \xrightarrow{k}$$

$$2n \, H_2O \; + \quad \underset{O}{\{O-R-O-\underset{\underset{O}{\|}}{C}-R'-\overset{O}{\overset{\|}{C}}\}_n}$$

$$Rate \; = \; - \frac{d[COOH]}{dt} \; = \; - \frac{d[OH]}{dt}$$

$$= \; - \frac{d[FG]}{dt}$$

$$- \frac{d[FG]}{dt} \; = \; k \, [COOH]^2 \, [OH]$$

$\quad$ $-(COOH)$ acts as both reactant and catalyst

$$= \; k \, [FG]^3$$

$$\Rightarrow \left\{ 1/[FG]^3 \right\} d \, [FG] \; = \; -k \, dt$$

$[FG]_0 = $ initial Concentration

$$\Rightarrow \int_{[FG]_0} \frac{d[FG]}{[FG]^3} \; = \; - \int_0^t k \, dt$$

$[FG] = $ Conc^n at time, t

$$\Rightarrow \; \frac{1}{[FG]^2} - \frac{1}{[FG]_0^2} \; = \; 2kt \qquad —①$$

$$Extent \; of \; reaction \quad P \; = \; \frac{[FG]_0 - [FG]}{[FG]_0}$$

$$\Rightarrow \; \frac{[FG]}{[FG]_0} \; = \; 1 - P$$

$$\Rightarrow \; [FG] \; = \; (1-P) \, [FG]_0$$

$$① \Rightarrow \; \frac{1}{[FG]_0^2 (1-P)^2} - \frac{1}{[FG]_0^2} \; = \; 2kt$$

$$\Rightarrow \; 2k \, [FG]_0^2 \, t \; = \; \frac{1}{(1-P)^2} - 1$$

$$Average \; degree \; of \; polymerisation$$

$$\overline{D_{pn}} \; = \; \frac{1}{1-P} \; = \; \frac{[FG]_0}{[FG]}$$

$$\overline{D_{Pn}}^2 = 2k\,[FG]_0^2\,t + 1$$

Kinetics of acid catalysed polymerisation

$$\text{Rate} = -\frac{d[FG]}{dt} = k_2[COOH][OH]$$

where $k_x = k[X]$

$[X]$ being the acid concn

$$-\frac{d[FG]}{dt} = k_x[FG]^2$$

$$\Rightarrow \quad -\frac{d[FG]}{[FG]^2} = k_x\,dt$$

$$\Rightarrow \quad -\int_{[FG]_0}^{[FG]}\frac{d[FG]}{[FG]^2} = \int_0^d k_x\,dt$$

$$\Rightarrow \quad \frac{1}{[FG]} - \frac{1}{[FG]_0} = k_x\,t \qquad -\textcircled{1}$$

$$\frac{[FG]_0 - [FG]}{[FG]_0} = P$$

$$\Rightarrow \quad [FG] = (1-P)[FG]_0$$

$$\textcircled{1} \Rightarrow \quad \frac{1}{(1-P)[FG]_0} - \frac{1}{[FG]_0} = k_x\,t$$

$$\Rightarrow \quad k_x[FG]_0\,t = \frac{1}{1-P} - 1$$

$$\overline{D_{pn}} = k_x[FG]_0\,t + 1$$

Careother's equation

Careothere proposed a relationship between the number-average degree of polymerisation $\overline{D}_{pn}$ and extent of reaction, P.

Let us assume N_0 is the number of molecule present initially and N is the number of molecule present after time, t

$$P = \frac{N_0 - N}{N_0} = 1 - \frac{N}{N_0}$$

$$\Rightarrow \frac{N_0}{N} = \frac{1}{1-P} \qquad — \textcircled{1}$$

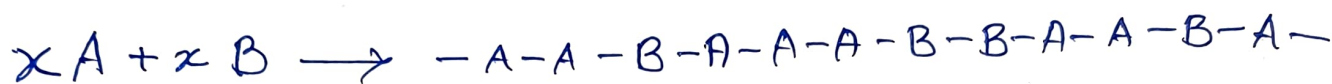Number average degree of polymerisation,

$$\overline{D}_{pn} = \frac{\text{Number of molecules present initially}}{\text{Number of molecules remain after time, } t}$$

$$= \frac{N_0}{N} \qquad — \textcircled{2}$$

$\textcircled{1}, \textcircled{2} \Rightarrow$

$$\overline{D}_{pn} = \frac{1}{1-P}$$

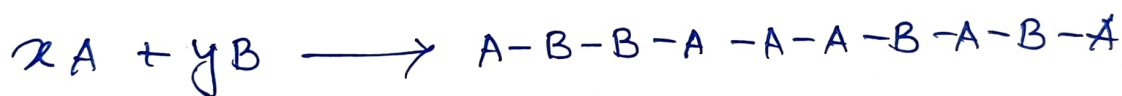# Copolymerisation

A mixture of two or more monomers get polymerised to yield as product. The product is known as Co-polymer.
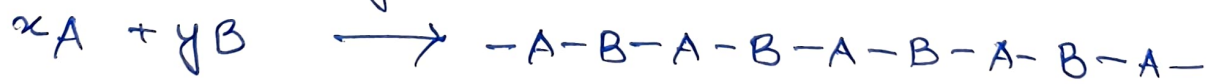
$$xA + xB \longrightarrow -A-A-B-A-A-A-B-B-A-A-B-A-$$

Classification

① Random copolymer — These are formed by the random arrangement of monomer units.

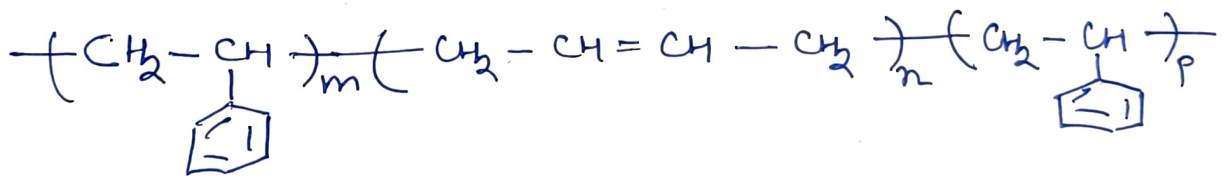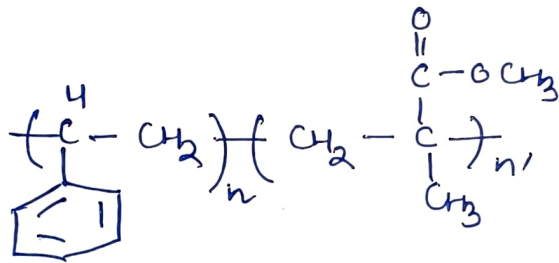$$xA + yB \longrightarrow A-B-B-A-A-A-B-A-B-A$$

② Alternating Co-polymer — These are linear Co-polymer in which monomers are arranged in alternating manner.
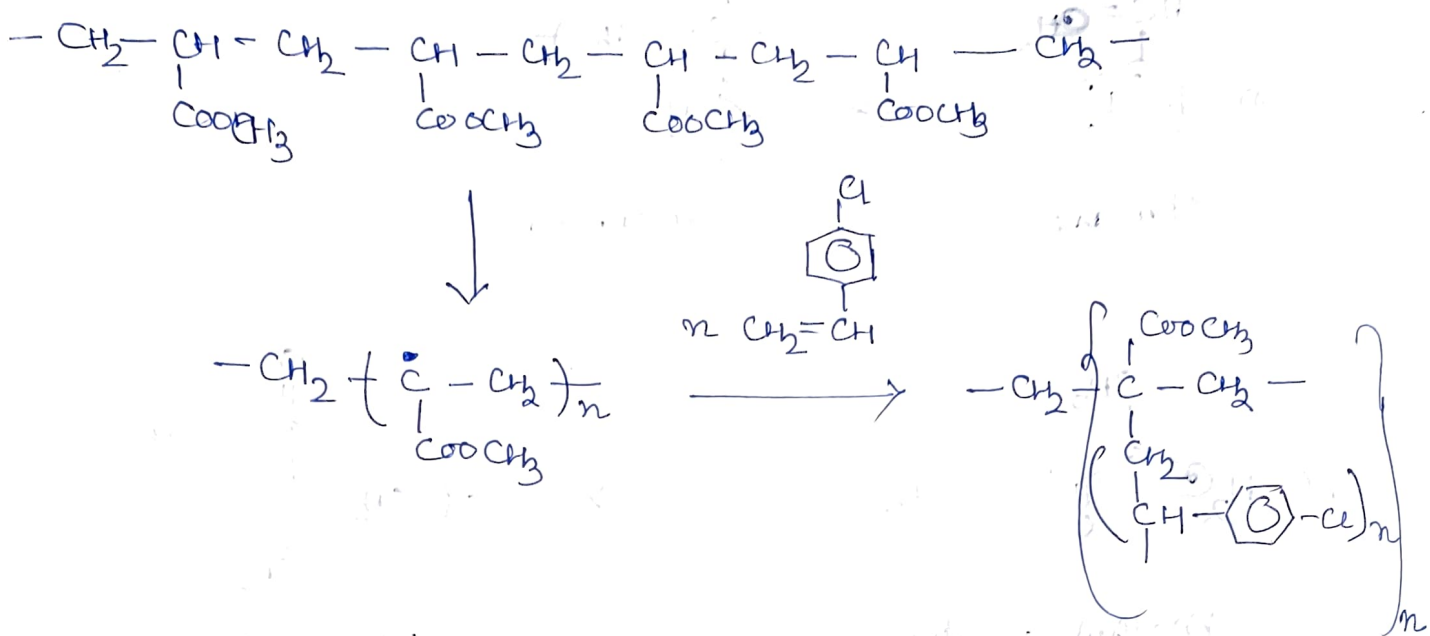
$$xA + yB \longrightarrow -A-B-A-B-A-B-A-B-A-$$

Example! Co-polymerisation of this type is mainly AA-BB type Condensation polymers.

③ Block Co-polymer — Block polymers are made by different polymerised monomer.

$$HC=CH_2$$

(iii) Styrene $\longrightarrow$ $\{\overset{H}{\underset{}{C}}-CH_2\}_n$ Polystyrene

n' $H_2C=\underset{O}{\overset{CH_3}{C}}-\overset{O}{\underset{O}{C}}-O-CH_3$ methyl methaacrylate $\longrightarrow$

Polymethyl methacrylate (PMMA)
$$\{CH_2-\underset{CH_3}{\overset{\overset{O}{\parallel}}{\underset{}{C}}-OCH_3}\}_{n'}$$

$\{\overset{H}{\underset{}{C}}-CH_2\}_n\{CH_2-\underset{CH_3}{\overset{\overset{O}{\parallel}}{\underset{}{C}}-OCH_3}\}_{n'}$

$$\{CH_2-CH\}_m\{CH_2-CH=CH-CH_2\}_n\{CH_2-CH\}_p$$
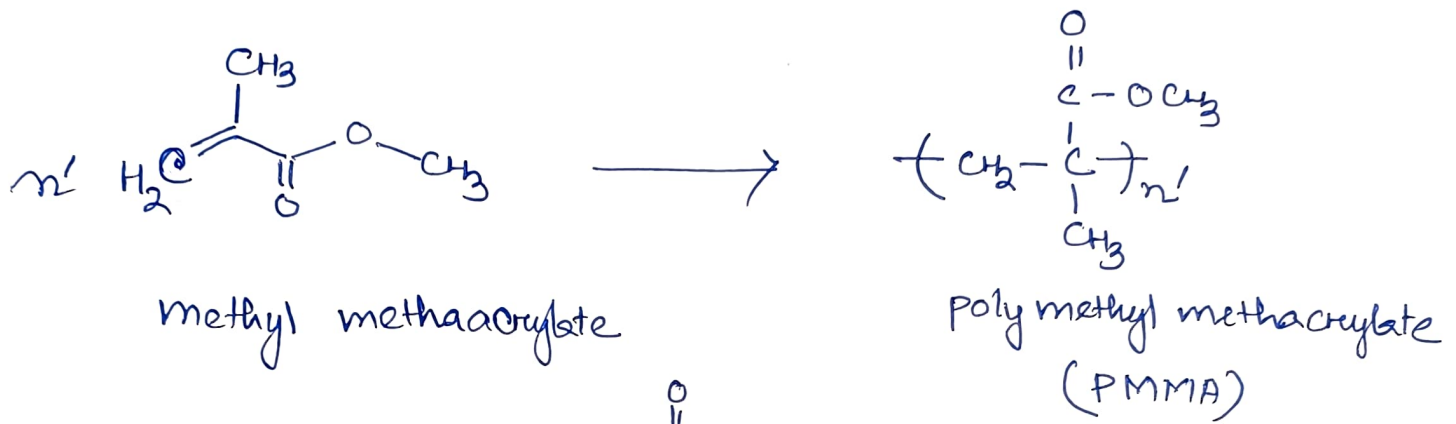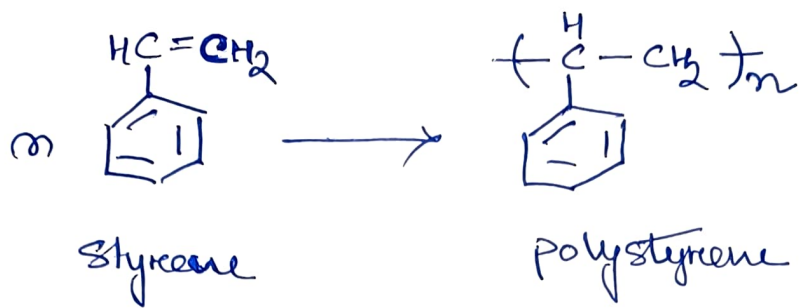
Styrene butadiene styrene (SBS)

(4) **Graft copolymer** – Graft co polymers are the polymers in which polymeric chain of one type of monomer is grafted on as a side chain to the backbone chain of another linear polymer.

The top shows a polymer structure and reaction scheme (chemical structures).

$-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-$

with pendant groups $COOCH_3$, $COOCH_3$, $COOCH_3$, $COOCH_3$

↓

$-CH_2-\left(\overset{\bullet}{C}-CH_2\right)_n$ with $COOCH_3$ group

$\xrightarrow{n\ CH_2=CH\ (\text{with } Cl\text{-substituted benzene ring})}$

product structure:

$-CH_2-\left(\overset{COOCH_3}{\underset{}{C}}-CH_2-\right)\left(\overset{CH_2}{\underset{CH-\bigcirc-Cl}{}}\right)_n$ all in brackets subscript n
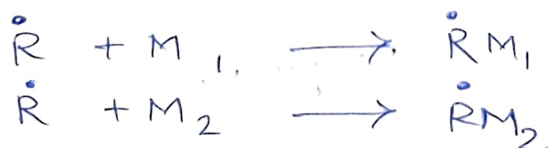
Kinetics

The determination of the copolymere composition is based on certain assumptions

(i) Propagation is the only reaction of importance, for it is repeated many times fore each initiation and termination step.
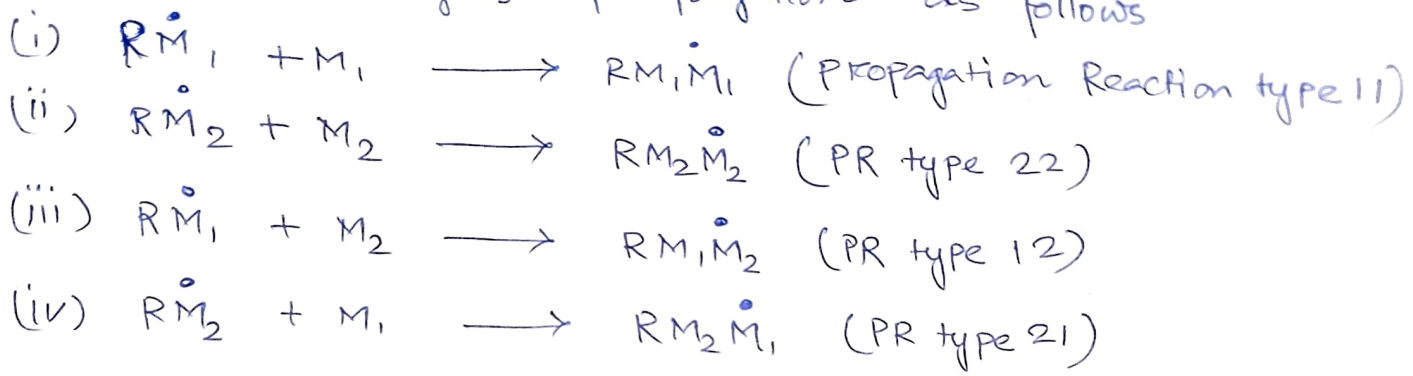
(ii) The chemical reactivity of propagating chain is dependent only on the last monomere unit.
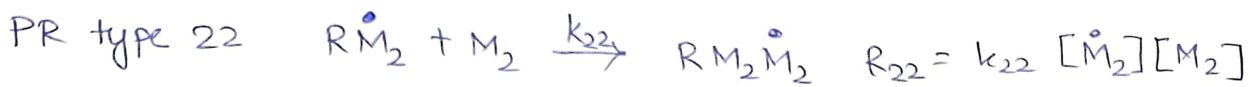
(iii) Steady state concentration assumption.

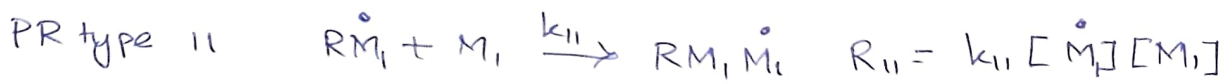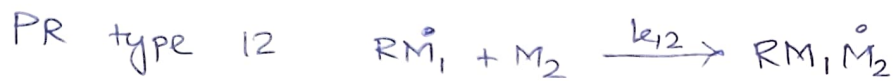Let us considere two monomers M_1 and M_2, polymerised in presence of a free radical initiatore $\overset{\bullet}{R}$.

$\overset{\bullet}{R} + M_1 \longrightarrow \overset{\bullet}{R}M_1$

$\overset{\bullet}{R} + M_2 \longrightarrow \overset{\bullet}{R}M_2$

Then it undergoes propagation as follows

(i) $R\dot{M}_1 + M_1 \longrightarrow RM_1\dot{M}_1$ (Propagation Reaction type 11)

(ii) $R\dot{M}_2 + M_2 \longrightarrow RM_2\dot{M}_2$ (PR type 22)

(iii) $R\dot{M}_1 + M_2 \longrightarrow RM_1\dot{M}_2$ (PR type 12)

(iv) $R\dot{M}_2 + M_1 \longrightarrow RM_2\dot{M}_1$ (PR type 21)

Homopolymerisation

PR type 11 $R\dot{M}_1 + M_1 \xrightarrow{k_{11}} RM_1\dot{M}_1$ $R_{11} = k_{11}[\dot{M}_1][M_1]$

PR type 22 $R\dot{M}_2 + M_2 \xrightarrow{k_{22}} RM_2\dot{M}_2$ $R_{22} = k_{22}[\dot{M}_2][M_2]$

Heteropolymerisation

PR type 12 $R\dot{M}_1 + M_2 \xrightarrow{k_{12}} RM_1\dot{M}_2$

PR type 21 $R\dot{M}_2 + M_1 \xrightarrow{k_{21}} RM_2\dot{M}_1$

$$-\frac{d[M_1]}{dt} = k_{11}[\dot{M}_1][M_1] + k_{21}[\dot{M}_2][M_1] \quad \text{———①}$$

$$-\frac{d[M_2]}{dt} = k_{22}[\dot{M}_2][M_2] + k_{12}[\dot{M}_1][M_2] \quad \text{———②}$$

The concentrations of both type of growing radicals M_1 and M_2 remain constant. For this, their rate of interconversion is equal.

$$k_{12}[\dot{M}_1][M_2] = k_{21}[\dot{M}_2][M_1]$$

$$\Rightarrow [\dot{M}_1] = \frac{k_{21}[\dot{M}_2][M_1]}{k_{12}[M_2]}$$

$$\frac{①}{②} \Rightarrow \frac{d[M_1]}{d[M_2]} = \frac{k_{11}[\dot{M}_1][M_1] + k_{21}[\dot{M}_2][M_1]}{k_{22}[\dot{M}_2][M_2] + k_{12}[\dot{M}_1][M_2]}$$

$$= \frac{\dfrac{k_{11}\,k_{21}[\dot{M}_2][M_1]^2}{k_{12}[M_2]} + k_{21}[\dot{M}_2][M_1]}{k_{22}[\dot{M}_2][M_2] + \dfrac{k_{12}\,k_{21}[\dot{M}_2][M_2][M_1]}{k_{12}[M_2]}}$$

(i) Alternating Co-polymere , k_{12} , $k_{21} \neq 0$

$$k_{11} , k_{22} = 0$$

$$r_1 = r_2 = 0$$

(ii) Random Copolymere $r_1 = r_2 = 1$

probability of all the polymerisation is the same.

(iii) Ideal Co-polymere $r_1 r_2 = 1$

$$\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

(iv) $r_1 > 1$, $r_2 < 1$ probability of M_1 enthering the polymere chain is more.

(v) $r_1 < 1$, $r_2 > 1$, probability of M_2 entering the polymere chain is more.

(vi) $r_1 = r_2 = \infty$ ie $k_{12} = k_{21} = 0$

Mixture of homopolymers