Macromolecules:

Macromolecules or polymers are very high molar mass compounds consisting of structural units inter connected by covalent bonds. Their molar mass vary from 5,000 to several millions. The chemistry of these giant molecules is known as polymer chemistry or macromolecular chemistry.

A polymer consists of a large number of simple monomeric structural units which are repeated over and over again to form a giant molecule called a macromolecule. The simple unit is called the repeat unit.

Degree of polymerization (P):

The length of the polymer chain is specified by the no. of repeat units in the chain. The no. of repeat units or the monomer unit in the chain is called degree of polymerization.

It is generally designated by the symbol, P.

The molar mass, M of the polymer is related to P by the equation. $P = \frac{M}{m}$, where m is the molar mass of monomeric units.

Molar Masses of Polymers:

① No. average molar mass ($\overline{M}_N$):

$$\overline{M}_N = \frac{\sum n_i M_i}{\sum n_i}$$

② Mass-average molar mass ($\overline{M}_M$):

$$\overline{M}_M = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

2016

Q. generally the mass average molar mass of a polymer is greater than its no. average molar mass. state ① when they become equal.

2017

Q. define no. average and mass average molar mass of polymers. ~~for~~ a sample of polymer, which one has a larger value and why? ③

Polydispersity Index (P.D.I.):

2015, 2017

Q. What Define polydispersity index of a polymer. (1)

$$P.D.I. = \frac{\overline{M}_M}{\overline{M}_N}$$

Note: If the sample is monodisperse (i.e. all the chains are identical), then $\overline{M}_M = \overline{M}_N$.

~~Condensation~~

Polymerization Reactions:

The polymerization reactions can be classified as —

(a) Condensation Polymerization:

A condensation polymer is a type of polymer in which the polymer contains fewer atoms less than the monomers from which the polymer is formed. In this process, the condensation takes place between two polyfunctional molecules to produce a large molecule.

e.g. (i) $n\ HO-CH_2-CH_2-OH$ + n HOOC–⟨o⟩–COOH

ethylene glycol — terephthalic acid

↓

$$\left(O-CH_2-CH_2-O-CO-\langle o\rangle-CO\right)_n + (2n-1)\ H_2O.$$

poly(ethylene terephthalate) or PET.

(ii) $n\ H_2N-(CH_2)_6-NH_2$ + $n\ HOOC-(CH_2)_4-COOH$

Hexamethylene diamine — adipic acid

↓

$$\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO\right]_n + 2n\ H_2O$$

Nylon 6,6.

* Nylon 66 and polyesters are the products of condensation polymerization.

2016

Q. Name the type of polymerization which results in Nylon-66. (1)

2016 (2)

Q. Write the different steps through which addition polymerization occurs

(b) Addition Polymerization:

Addition or chain reaction or vinyl polymers are formed from monomers containing double bonds. It involves chain reactions in which the chain ~~rea~~ carrier may be an ion or a reactive substance with one unpaired e- called a free radical. A free radical is generally formed by the decomposition of the initiator.

e.g. Vinyl polymerization involves three steps —

(i) Initiation (ii) Propagation (iii) Termination.

(i) Initiation: It involves two steps —

(a) The first step is the decomposition of the initiator to produce a free radical.

$$I - I \longrightarrow 2I^{\bullet} \text{ (free radical)}$$

(b) In the second step, the free radical interacts with the vinyl monomer to give rise the initiated monomer radical.

$$I^{\bullet} + CH_2 = CHR \xrightarrow{K_i} I - CH_2 - \overset{\bullet}{C}H - R$$

vinylmonomer (M')

(ii) Polymerization or Propagation:

Here, a new radical adds up to the monomer molecules in rapid succession to form a growing polymer chain.

$$I - CH_2 - \overset{\bullet}{C}H - R + CH_2 = CHR \xrightarrow{K_p} I - CH_2 - CHR - CH_2 - \overset{\bullet}{C}H - R$$

$$I - CH_2 - CHR - CH_2 - \overset{\bullet}{C}H - R + CH_2 = CHR \xrightarrow{K_p} I - CH_2 - CHR - CH_2 - \underset{\underset{R - \overset{\bullet}{C}H - CH_2}{|}}{CHR}$$

$$I - CH_2 - CHR - CH_2 - CHR - CH_2 - \overset{\bullet}{C}HR + n\,CH_2 = CHR \xrightarrow{K_p} I\left\{CH_2 - CHR\right\}_{n+2} CH_2 - \overset{\bullet}{C}HR$$

(iii) Termination:

In this step, the growing chain radical deactivates either by combination ~~of~~ or by disproportionation to form a dead polymer.

ⓐ Combination :

$$\sim CH_2-\dot{C}HR + \dot{C}HR-CH_2\sim \xrightarrow{K_t} \sim CH_2-CHR-CHR-CH_2\sim$$

dead polymer.

ⓑ Disproportionation:

$$\sim CH_2-\dot{C}HR + R\dot{C}H-CH_2\sim \xrightarrow{K_t} \sim CH_2-CH_2R + CHR=CH$$

dead polymer

LDPE and HDPE :

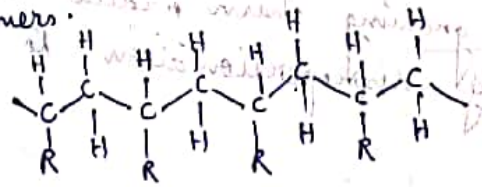
Polyethylene is commercially available in two grades: Low-density polyethylene (LDPE) and High-density polyethylene (HDPE). LDPE consists of several short and long branches while HDPE consists of linear unbranched chains. ~~as shown below~~ Since HDPE is almost unbranched, its chains can be close-packed in the solid state. Such close packing would not be possible in the case of branched LDPE. Hence, HDPE has higher density than LDPE. LDPE is used for the fabrication of pipes, wires, containers and cable insulation while HDPE is used for making industrial containers. HDPE is stronger and chemically more inert than LDPE.

2014

Q. Polyethylene is commercially available in two forms — low density polyethylene and high density polyethylene. State the difference in structure because of which the two differ in density.

Classification of polymers:

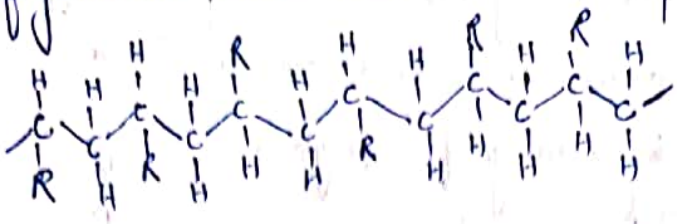
① Isotactic polymers: Polymers in which all the asymmetric carbon atoms have the same (d- or l-) configuration are called isotactic polymers.



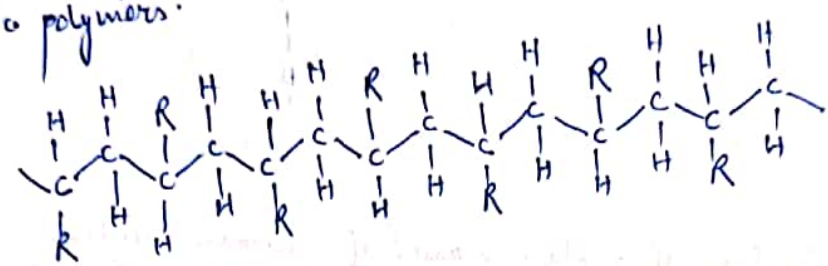
2017

Q. State what do you mean by Isotactic polymer. ①

② Atactic polymers: Polymers having random sequences of d- and l- configurations are known as atactic polymers. ~~the plane~~



③ Syndiotactic polymers: Polymers having regular alternation of d- and l- configurations in the molecular chains are called syndiotactic polymers.



* Isotactic and syndiotactic polymers are collectively called stereoregular polymers. They are always arranged in a head-to-tail (α, β) arrangement.

Copolymers:

Copolymers are polymers which consist of monomeric units of different composition arranged at random in the polymeric chain as shown below:

.....—A—A—B—A—B—B—A—A—B—A—.....

where, A and B are the monomeric units of different composition, e.g. Proteins, nucleic acids and mixed polysaccharides.

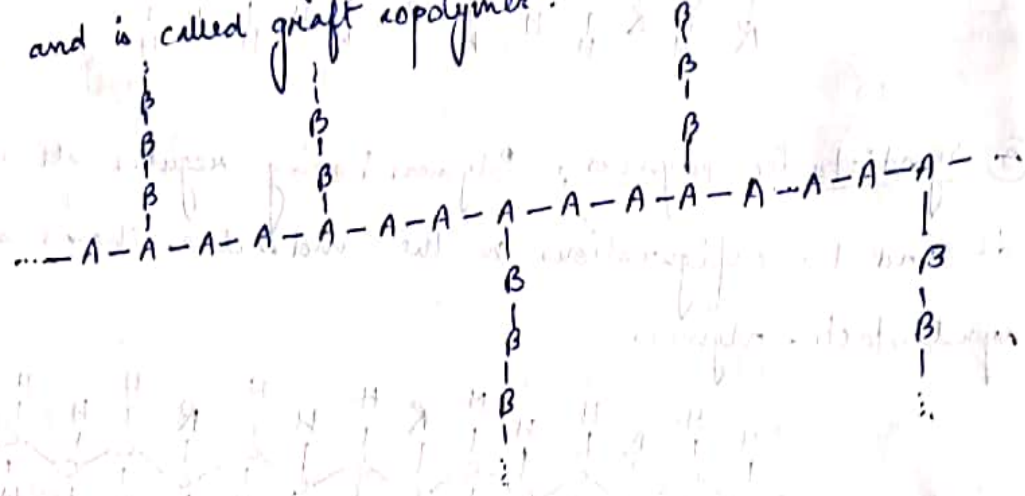
① Block copolymers:

If in a copolymer, the different monomeric units in the polymeric chain are not arranged at random but as alternations of runs of them as shown, it is called a block copolymer:

.....—A—A—A—A—B—B—B—B—A—A—A—A—.....

② Graft copolymers:

In some branched polymers, branches of a different monomeric species can be added i.e grafted on to linear chain of the polymer and is called graft copolymer.



Determination of molar masses of macromolecules:

2015. Marks=5

① Viscometry:

The viscosity average molecular weight (M_v) is obtained by this technique introduced by Staudinger. Since accurate measurement of absolute viscosity is difficult, it is convenient to measure relative viscosity, η_{rel}, defined as:

$$\eta_{rel} = \frac{\eta}{\eta_0} \longrightarrow (i)$$

where η and η_0 are the viscosity of the solution and the viscosity of the solvent respectively. Also,

$$\eta_{sp} = \eta_{rel} - 1 \longrightarrow (ii)$$

$$\eta_{red} = \frac{\eta_{sp}}{c} \longrightarrow (iii)$$

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c}\right) \longrightarrow (iv)$$

where η_{sp} is specific viscosity, η_{red} is reduced viscosity and $[\eta]$ is intrinsic viscosity (viscosity no. or Staudinger index). c is the concentration of the polymer.

Einstein derived the following relation between the viscosity of a dilute suspension of hard spherical molecules and the volume fraction, ϕ, of the solute molecules.

$$\eta = \eta_0 (1 + 1.25\,\phi) \longrightarrow (V)$$

$$\Rightarrow \eta/\eta_0 - 1 = \eta_{sp} = 2.5\,\phi \longrightarrow (VI)$$

$\therefore$ Eqn (IV) & (VI) $\Rightarrow [\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c}\right) = \frac{2.5\,\phi}{c} \longrightarrow (VII)$

Two equations are obtained by plotting η_{sp}/c and $\ln \eta_{red}/c$ versus c which give straight lines.

Huggin's equation : $\eta_{sp}/c = [\eta] + K'[\eta]^2 c \longrightarrow (VIII)$

Kraemer's equation : $\ln \eta_{red}/c = [\eta] - K''[\eta]^2 c. \rightarrow (IX)$

Again, Staudinger found that for a series of samples of the same polymer in a given solvent and at a constant temperature, the intrinsic viscosity is related to the molar mass of the polymer by the following equation known as Mark-Kuhn-Houwink-Sakurada equation, formerly called Staudinger eqn:

$$[\eta] = K(\overline{M}_{visc})^a \longrightarrow (X)$$

Where, $\overline{M}_{visc}$ is the viscosity-average molar mass of the polymer and 'K' and 'a' are constants. The value of 'a' depends upon the geometry or the shape of the macromolecule. The value of 'a' vary from 0.5 to 1.

Taking log in eqn (X),

$$\ln [\eta] = \ln K + a \ln \overline{M}_{visc} \longrightarrow (XI)$$

Eqn (XI) shows that a log-log plot of $[\eta]$ vs $\overline{M}_{visc}$ gives a straight line with slope equal to a and intercept equal to ln K. Thus knowing the values of a and K from the graph, the viscosity-average molar mass $\overline{M}_{visc}$ can be determined from intrinsic viscosity measurements.

② **Osmometry:**

Osmotic pressure measurements are used for studying macromolecules because osmotic changes are larger than the changes in boiling point elevation, freezing point depression and vapour pressure lowering.

If π is the osmotic pressure of a solution in which the mole fraction of the solvent is x_1, then, the condition for equilibrium for the chemical potential of the solvent on both sides of the semipermeable membrane gives,

$$RT \ln \gamma_1 x_1 + \pi \bar{V}_1 = 0. \longrightarrow (I)$$

where, γ_1 is the activity coefficient of the solvent and $\bar{V}_1$ is the partial molar volume of the solvent in the solution. For a dilute solution, $x_1 \longrightarrow 1$ and $\bar{V}_1 \longrightarrow V_1^\circ$, the molar volume of the pure solvent. If we replace ~~by~~ x_1 by $(1-x_2)$ where x_2 is the mole fraction of the solute, then,

$$\pi V_1^\circ = RT\left(x_2 + x_2^2/2 + x_2^3/3 + \dots\right). \longrightarrow (II).$$

For a polymer soln of concn c,

$$x_2 = \frac{c/M}{1/V_1^\circ + c/M} \approx \frac{V_1^\circ c}{M} \quad \text{for a dilute soln.} \longrightarrow (III)$$

where M is the molar mass of the polymer.

Substituting the value of x_2 in eqn (II) we get,

$$\frac{\pi}{c} = \frac{RT}{M}\left[1 + 1\left(\frac{V_1^\circ}{M}\right)c + \frac{1}{3}\left(\frac{V_1^\circ}{M}\right)^2 c^2 + \dots\right] \longrightarrow (IV).$$

Eqn (IV) is of the form,

$$\frac{\pi}{c} = \frac{RT}{M}\left(1 + A_2 c + A_3 c^2 + \dots\right) \longrightarrow (V)$$

$$\Rightarrow \frac{\pi}{c} = RT\left(\frac{1}{M} + B_2 c + B_3 c^2 + \dots\right) \longrightarrow (VI).$$

where, B_2, B_3, etc. are the second, third, etc. virial coefficients. Equ (vi) is the Van't Hoff eqn. The quantity $\frac{\pi}{c}$ is called reduced osmotic pressure. If B_3c^2 is neglected, a graph of $\frac{\pi}{c}$ vs c would be a straight line which when extrapolated to $c=0$ gives $\frac{RT}{M}$ as the intercept on the $\frac{\pi}{c}$ axis. i.e. $\lim_{c \to 0} \left(\frac{\pi}{c}\right) = \frac{RT}{M}$.

From the intercept, the molar mass M can be easily calculated.

2014, 2016, 2018

Q. Discuss the osmotic pressure (osmometry) method for determination of molar mass of polymers. Why does this method give no. average molar mass only? 4+1 = (5).

Ans: The osmotic pressure measurement leads to no. average molar mass because osmotic pressure is a colligative property which depends upon the no. of molecules of the polymer and not on their mass and all molecules whether heavy or light make equal contribution.

Light Scattering Method:

It is used to determine the mass average or weight average molecular weight (M_w) of a polymer. When polarizable particles are placed in the oscillating electric field of a beam of light, the light scattering occurs. This method depends on the light, when the light is passing through polymer solution, it is measured by loss of energy because of absorption, conversion to heat and scattering. The intensity of scattered light relies on the

concentration, size and polarizability which depends on the molecular weight.

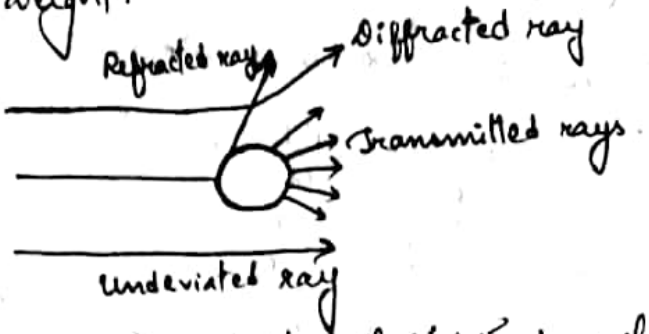


Fig. Modes of scattering of light in solution

For light scattering measurements, the total amount of the scattered light is deduced from the decrease in intensity of the incident beam, I_0, as it passes through a polymer sample. This can be described in terms of Beer's law for the absorption of light, which is as follows:

$$\boxed{\frac{I}{I_0} = e^{-\tau l}}$$

Where τ is the measure of the decrease of the incident beam intensity per unit length l and is called turbidity of the solⁿ.

The intensity of scattered light or turbidity (τ) is proportional to the square of the difference between the index of refraction (n) of the polymer solⁿ and of the solvent n_0 to the molecular weight of the polymer (M) and to the inverse fourth power to the wavelength of light used (λ). Thus,

$$\frac{Hc}{\tau} = \frac{1}{M_w P_\theta}\left(1 + 2Bc + Cc^2 + \dots\right).$$

where,

$$H = \frac{32\pi^2}{3} \cdot \frac{n_0^2 \left(dn/dc\right)^2}{\lambda^4 N}$$

$$\tau = K' n^2 \left(\frac{i_{90}}{i_0}\right).$$

where, n_0 is refractive index of the solvent, n is refractive index of the soln, c is concentration; B, C, etc. are virial constants, P is the particle scattering factor and N is Avogadro's number. The expression $\frac{dn}{dc}$ is the specific refractive increment and is determined by taking the slope of the refractive index readings as a function of polymer concentration.

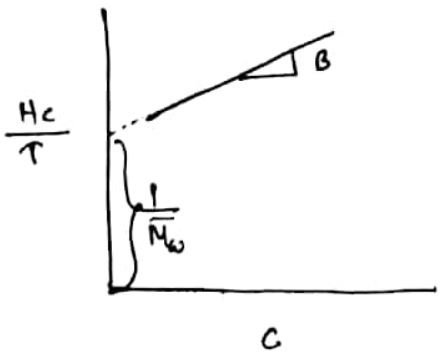
Several expressions are generally used in describing the relationship between values measured by light scattering photometry and molecular weight.

$$\frac{Kc}{R} = \frac{1}{M_w}\left(1 + 2Bc + Cc^2 + \cdots\right).$$

At low conc^n of polymer sol^n, the above eqn reduces to an eq^n of a straight line.

$$\frac{Hc}{T} = \frac{1}{\overline{M}_w} + \frac{2Bc}{\overline{M}_w}$$

When a graph is plotted between $\frac{Hc}{T}$ as the y-axis vs c as the x-axis, a straight line will be obtained with $\frac{1}{\overline{M}_w}$ as the intercept on extrapolation and the slope will be B.



2017

Q. Discuss the light scattering method for determination of the molar mass of polymer. (5)

Kinetics of addition polymerization:

Let us consider the catalytic polymerization of a monomer, M say, $CH_2 = CHX$ where X = halogen. The following stages are involved in this process.

Step 1: Initiation: Formation of free radical R from initiator I.

$$I \xrightarrow{K_1} R$$

where K_1 is the rate constant for the initiation process. The rate of production of the free radical is given by:

$$r = K_1[I] \longrightarrow (I)$$

Step 2: Propagation: The free radical R adds to the double bond of the monomer molecule generating new free radicals:

$$CH_2 = CHX + R \xrightarrow{K_2} RCH_2CHX$$

$$RCH_2CHX + CH_2 = CHX \longrightarrow R-(CH_2-CHX)_2 \text{ and so on.}$$

The rate of disappearance of the monomer M is given by

$$-\frac{d[M]}{dt} = K_2[R][M] \longrightarrow (II)$$

These steps are of second order and very rapid.

Step 3: Termination: It is achieved by the recombination of two free radicals.

$$R-(CH_2-CHX)_n + (XCH-CH_2)_n-R \xrightarrow{K_3} R-(CH_2-CHX)_n-(XCH-CH_2)_n-R$$

Applying steady state approximation,

$$K_1[I] = K_3[R]^2 \longrightarrow (III)$$

$$\Rightarrow [R]^2 = \frac{K_1[I]}{K_3}$$

$$\Rightarrow [R] = \left(\frac{K_1}{K_3}\right)^{\frac{1}{2}}[I]^{\frac{1}{2}} \longrightarrow (IV)$$

Putting the value of [R] in eqn (11),

$$-\frac{d[M]}{dt} = k_2 \cdot \left(\frac{k_1}{k_3}\right)^{\frac{1}{2}} \cdot [I]^{\frac{1}{2}} [M].$$

$$= K [I]^{\frac{1}{2}} [M].$$

Two factors can be calculated from the above equation

(a) Kinetic chain length (γ):

It is the ratio of the overall rate to the rate of the initiation step. It can also be defined as the no. of repeating chain units in the polymer chain.

$$\gamma = \frac{-d[M]/dt}{r} = \frac{-d[M]/dt}{k_1 [I]}.$$

(b) Probability (p):

Probability p for the addition of another monomer to the growing chain radical is given by.

$$p = \frac{k_2 [M]}{k_2 [M] + k_3 [R]} = \frac{1}{1 + \frac{(k_1 k_3)^{\frac{1}{2}} [I]^{\frac{1}{2}}}{k_2 [M]}}.$$

e.g. In vinyl polymerization, p is of the order of 0.999.

2014, 2017

Q. Discuss the kinetics of addition polymerization. (5)

Kinetics of Condensation polymerization:

Polymerizn:

Step 1: The first step is the reaction of a diol and a diacid to form a dimer.

$$HO-R-OH + HOOC-R'-COOH \longrightarrow \underset{\text{Dimer.}}{HO-R-O-CO-R'-COOH} + H_2O$$

Step 2:

The dimer may react with the diol forming a trimer

$$HO-R-OCO-R'-COOH + HO-R-OH \longrightarrow \underset{\text{Trimer}}{HO-R-OCO-R'-COO-R-OH} + H_2O$$

Step 3:

The dimer may react with a diacid monomer forming a trimer.

$$HO-R-OCO-R'-COOH + HOOC-R'-COOH$$

$$\downarrow$$

$$\underset{\text{Trimer}}{HOOC-R'-COO-R-COO-R'-COOH} + H_2O$$

Step 4:

Two dimer molecules may react with each other forming a tetramer.

$$HO-R-O-CO-R'-COOH + HO-R-OCO-R'-COOH$$

$$\downarrow$$

$$\underset{\text{Tetramer}}{HO-R-OCO-R'-COO-R-COO-R'-COOH} + H_2O$$

In subsequent steps, the trimer and tetramer either reacts with themselves or with the monomer forming the growing polymer. Hence, the ~~polymer~~ size of polymer molecule increases at a relatively slow rate in case of condensation polymerization.

Kinetics

Step 1: Protonation of the acid.

$$\sim\!C(=O)-OH + H^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \sim\!C^{\oplus}(OH)-OH \longrightarrow (1)$$

Step II: Addition of diol with acid. It is the slowest step

$$\sim\sim\overset{OH}{\underset{\oplus}{C}}-OH + \sim\sim R'-OH \underset{K_4}{\overset{K_3}{\rightleftharpoons}} \sim\sim\overset{OH}{\underset{\sim\sim OH}{C}}-OH \longrightarrow (ii)$$

Step III: deprotonation of the moiety.

$$\sim\sim\overset{OH}{C}-OH + \sim\sim R'-OH \underset{K_6}{\overset{K_5}{\rightleftharpoons}} HOOC-R-COO-R'-OH + \sim\sim COO\sim\sim + H_2O + H^+ \longrightarrow (iii).$$

Rate of polymerization:

$$r_p = \frac{-d[COOH]}{dt} = K_3[\overset{+}{C}OOH_2][OH] \longrightarrow (1).$$

$$K = \frac{k_1}{k_2}$$

$$\Rightarrow K = \frac{[\overset{+}{C}OOH_2]}{[COOH][H^+]}.$$

$$\Rightarrow [\overset{+}{C}OOH_2] = K[COOH][H^+] \longrightarrow (2).$$

From eqn (1) and (2), we get,

$$r_p = KK_3[COOH][OH][H^+].$$

$$\boxed{\Rightarrow r_p = K'[COOH][OH][H^+]} \longrightarrow (3).$$

Eqn (3) is the rate expression for condensation polymerization.

Note: In self catalysed condensation polymerization,

$$r_p = K'[COOH][OH][COOH].$$

$$= K'[COOH]^2[OH] \longrightarrow (4).$$

Let, $[COOH] = [OH] = c$.

Again, In acid catalysed condensation polymerization,

$$r_p = K'[COOH][OH] \longrightarrow (5).$$

$$\Rightarrow r_p = K'c^2$$

$$\Rightarrow r_p = \frac{-d[COOH]}{dt}$$

$$\Rightarrow r_p = \frac{-dc}{dt}$$

$$\cancel{\Rightarrow r_p = 1}$$

$$\therefore \frac{-dc}{dt} = k'c^2$$

$$\Rightarrow -\int_{c_0}^{c_t} \frac{dc}{c^2} = k' \int_0^t dt$$

$$\Rightarrow \left[\frac{1}{c}\right]_{c_0}^{c_t} = kt.$$

$$\Rightarrow \left[\frac{1}{c_t} - \frac{1}{c_0}\right] = kt$$

$$\Rightarrow k = \frac{1}{t}\left[\frac{1}{c_t} - \frac{1}{c_0}\right].$$

Again, Eqn (4) $\Rightarrow r_p = k'c^3$.

$$\Rightarrow r_p = \frac{-d[COOH]^2}{dt}$$

$$\Rightarrow r_p = \frac{-dc^2}{dt}.$$

$$\therefore -\frac{dc^2}{dt} = k'c^3.$$

$$\Rightarrow -\frac{dc^2}{c^3} = k'.dt$$

$$\Rightarrow -\int_{c_0}^{c_t} \frac{dc^2}{c^3} = k'\int_0^t dt.$$

$$\Rightarrow \frac{1}{2}\left[\frac{1}{c_t^2} - \frac{1}{c_0^2}\right] = kt$$

$$\Rightarrow k = \frac{1}{2t}\left[\frac{1}{c_t^2} - \frac{1}{c_0^2}\right].$$