U-II

2008

Condensation / Step polymerisation

1. Poly condensation polymerisation
2. Poly addition polymerisation
3. Ring opening polymerisation

① Poly condensation polymerisation →
when the monomers contains active functional group (generally two) which react together with the elimination of a simple molecule such as H_2O, NH_3 then the product formed is called condensation polymer and this phenomenon known as Poly condensation polymerisation.

Exa: Nylon66:
which is formed by Hexamethylene diamine and adipic acid

$$NH_2-(CH_2)_6-NH_2 + COOH-(CH_2)_4-COOH$$

$$\downarrow -H_2O$$

$$NH_2-(CH_2)_6-NH-CO-(CH_2)_4-COOH$$

formed product can react further either amine or acid because both side groups are free
then last product is Nylon 66

Kinetics of Polycondensation ⇒

In polycondensation reaction the reactivity of function group is independent of the molecular size.

$$n\ A-A + n\ B-B \longrightarrow A-(AB)_{2n-1}-B + by\ product$$

To derive a mathmathetical expression we take a example - The synthesis of polyester from a dicarboxylic acid & a diol.

① Self-catalysed esterification ⇒

This reaction is catalysed by mineral acids, but in the absence of mineral acid (such as H_2SO_4, HCl) the reactant carboxylic acid itself act as catalyst for each step of reaction b/w hydroxyl group & -COOH group.

$$-COOH + -OH \xrightarrow[\text{catalyst}]{+COOH} -COO^- + H_2O$$

⇒ The rate of the reaction can be measured by measuring the rate of disapperance of the carboxylic group.

$$-\frac{d[COOH]}{dt} = K [COOH]^2 [OH]$$

K = rate constant (considering equimolar presence of COOH & OH group)

C = concentration of each group at a given point.

$$-\frac{dc}{dt} = K [c]^2 [c]$$

$$-\frac{dc}{dt} = Kc^3$$

on integrating within the limits of $C_0 \to C$ $(t_0 \to t)$ we get

$$-\int_{C_0}^{C} \frac{dc}{c^3} = \int_0^t K \cdot dt \quad \text{— (1)}$$

~~on integration eq (1)~~

$$2Kt = \frac{1}{C^2} - \text{constant} \quad \text{— (2)}$$

where C_0 = initial concent.

extent of fraction = P

i.e fraction of a given functional group that has reacted at time t then

$$2Kt = \frac{1}{C^2} - \text{Constant}$$

$$\frac{C_0 - C}{C_0} = P$$

$$1 - \frac{C}{C_0} = P$$

$$1 - P = \frac{C}{C_0}$$

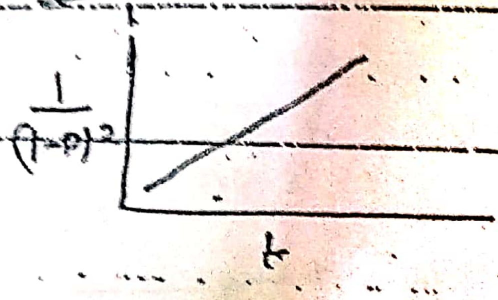
$$C = C_0 (1-P) \quad \text{--- (3)}$$

Combining eq (2) & (3)

$$2Kt = \frac{1}{[C_0^2 (1-P)^2]} - \text{Constant}\, \frac{1}{[C_0]^2}$$

$$\boxed{2 C_0^2 K t = \frac{1}{(1-P)^2} - \cancel{\text{Constant}}} \quad \text{--- (4)}$$

This implies that a graphical plot of $\frac{1}{(1-P)^2}$ vs t must be linear



for a simple esterification reaction, which proceeds without any side reaction, the number average of polymerisation may be related to P extent of polymerisation.

$$\bar{D}P_n = \frac{1}{1-P} = \frac{[C_0]}{[C]}$$

$$\bar{D}_P^2 = 2KC_0^2 t + 1$$

(1) Polyesterification using strong acids as catalyst

In this case the rate of disappearance of COOH groups can be then be expressed as

$$-\frac{d(COOH)}{dt} = k'(COOH)(OH)$$

$$-\frac{dc}{dt} = kc^2$$

$$C = C_0(1-P)$$

$$\boxed{C_0 kt = \frac{1}{(1-P)} - 1}$$

(2) Poly addition polymerisation ⇒

Poly addition polymerisation is brought about by the migration of atoms from one monomer unit to another or to the intermediate product.

For Exa: styrene can be polymerised in the presence of perchloric acid as follows.

$$CH_2{=}\underset{C_6H_5}{CH} + CH_2{=}\underset{C_6H_5}{CH} \longrightarrow CH_3\cdot\underset{C_6H_5}{CH}-\underset{C_6H_5}{CH}{=}CH$$

$$\downarrow\ n\,CH_2{=}\underset{C_6H_5}{CH}$$

$$CH_3-\underset{C_6H_5}{CH}-\left(CH_2\cdot\underset{C_6H_5}{CH}\right)_{n-1}-CH{=}\underset{C_6H_5}{CH}$$

C_0kt+1

ie, it will faster than polycondensation without acid catalyst.