Extent degree of Polymerisation :-

or stichiometric of reactant and degree of polymerisation

→ In polycondensation reaction two reactant are present in staichiometric equivalence

→ If there is a stoichiometric imbalance that is one of the reactant is present in the excess quantity. Then this imbalance

will show up on degree of polymerisation $\overline{DP}$

Consider a $RA_2 + RB_2$ polymerisation in which RB_2 is present in excess.

Reactant ratio r: (The ratio of the numbers of the different functional gps present initially.)

N_A = No. of reactive gp A-A

N_B = No. of reactive gp B-B

r = reactant ratio

$$r = \frac{N_A}{N_B} \quad -⑥$$

for linear step polymerisation

$N_A < N_B$ ... $r \leq 1$

Now:

No. of reactive gps of A to start with = $2N_A$

〃 〃 〃 B 〃 〃 = $2N_B$

So Total No. of reactive gp = $2N_A + 2N_B$ -⑦

from eq. ⑥ $N_B = \frac{N_A}{r}$

Putting this value in equation ⑦

~~$2N_A + 2N_B = 2N_A + \frac{2N_A}{r}$~~

Total No. of reactive gp

$$2(N_A + N_B) = 2N_A\left(1 + \frac{1}{r}\right) \quad -⑧$$

If The fraction of gp B consumed = rp

A = p

P is extent of reaction

we know that

$r \leq 1$ (equal or less than 1)

So,

the fraction of g.p. A remained unreacted $= 1-P$

and the fraction of g.p B remained unreacted $= 1-rP$

Total No of g.p remained unreacted =

$$\boxed{2N_A(1-P) + 2N_B(1-rP)} \quad -(9)$$

Now the degree of polymerization is given by

$$\bar{D}_p = \frac{[C_0]}{[C]} = \frac{2N_A\left(1+\frac{1}{r}\right)}{2N_A(1-P)+2N_B(1-rP)}$$

$$\boxed{\bar{D}_p = \frac{r+1}{r+1-2rP}}$$

* When no stoichiometric imbalance (i.e. both the reactants are present in stoichiometric equivalents)

$r=1$ and $\boxed{\bar{D}_p = \frac{1}{1-P}}$

When extent of conversion = 1 i.e. Polymerization goes to 100% completion $P=1$ then

$$\boxed{\bar{D}_p = \frac{1+r}{1-r}}$$

Unit III

CAROTHER'S-EQUATION

Carother developed a simple method of analysis for predicting the molar mass of polymers prepared by step polymerisation

If f = average functionality
P = Extent of reaction
$\bar{X}_n$ = average degree of polymerisation

Let N_0 be the total Number of reacting molecules initially present, giving an average functionality for the system as f

Let N be the Number of molecules present at time t when the extent of reaction is P

Then, number of molecules lost during the process over the time period t

$$t = (N_0 - N) ;$$

for each molecule lost, the number of functional groups lost is 2 (one of each kind) and hence the total number of functional gps lost is $2(N_0 - N)$ against the initial total number of $N_0 f$ functional gps.

$$\text{Extent of reaction } (P) = \frac{2(N_0 - N)}{N_0 f}$$

$$P = \frac{2}{f}\left(1 - \frac{N}{N_0}\right) \quad \text{—①}$$

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

$\frac{N_0 + N}{N_0}$

The average degree of polymerisation = $\bar{X}_n$ or $\bar{DP}_n$

$$\bar{X}_n \text{ or } \bar{DP}_n = \frac{N_0}{N} \quad \text{---(2)}$$

$$= \frac{\text{Number of molecules present initially}}{\text{Number of molecules reacting at time } t}$$

Combining equation (1) & (2)

$$\boxed{P = \frac{2}{f}\left(1 - \frac{1}{\bar{DP}_n \text{ or } \bar{X}_n}\right)} \quad \text{---(3)}$$

This is carother equation.

for bifunctional groups $f = 2$.

$$P = \left(1 - \frac{1}{\bar{X}_n}\right)$$

$$\text{or } \boxed{\bar{X}_n = \frac{1}{1-P}} \quad \text{---(4)}$$

This equation is applicable to $RA_2 + RB_2$, RAB and M_2 polymerisation, in which there is an exact stoichiometry balance in the number of reactive functional gp.

If the mean molecular weight of the repeat unit in the polymer molecule is $= M_0$

Then average molecular weight

$$\boxed{\bar{M}_n = \bar{X}_n \cdot M_0 = \frac{M_0}{(1-P)}} \quad \text{---(5)}$$