

Already discussed in Class
related to L1 (1)

$$f=1$$

Polysulphide $\sim S \sim$
 Polyester $\sim \text{COO} \sim$
 Polycarbonate $\sim \text{O} \sim \text{C} \sim \text{O} \sim$

Polyester ---CO---
 Polycarbonate ---O---CO---

Polyamide: $\text{---} \text{C}(=\text{O}) \text{---} \text{NH} \text{---}$
 Polyurethane: $\text{---} \text{NH} \text{---} \text{C}(=\text{O}) \text{---} \text{O} \text{---}$

Reaction: $\text{HOOC} \text{---} \text{R}_1 \text{---} \text{C}(=\text{O}) \text{OH} + n \text{H}_2\text{N} \text{---} \text{R}_2 \text{---} \text{NH}_2 \longrightarrow \text{HO} \left[\text{C}(=\text{O}) \text{---} \text{R}_1' \text{---} \text{C}(=\text{O}) \text{---} \text{NH} \text{---} \text{R}_2 \text{---} \text{NH} \right]_n + (2n-1) \text{H}_2\text{O}$
 where $\text{R}_1 = 4$, $\text{R}_2 = 6$ (nylon-6,6)

Polyurea $\sim \text{NH}-\text{CO}-\text{NH} \sim$

$f = 2$; OC(=O)c1ccc(cc1)C(=O)O + OCCO \rightarrow OC(=O)c1ccc(cc1)C(=O)OCCO + H_2O
 terephthalic acid ethylene glycol

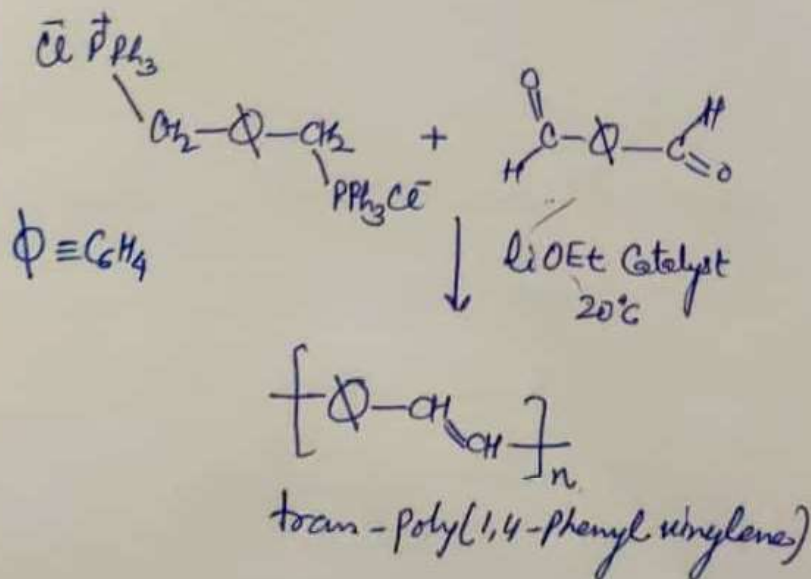
$RA_2 + RB_2 \rightarrow$ ~~ARB~~ | ARB Step Polymerization
 mutually reactive functional group. | W hydroxy Carboxylic acid
 Definition of A or B

Stoichiometric proportion of both the monomers are important. If one monomer present in excess, may kill the reaction and group of another monomer.

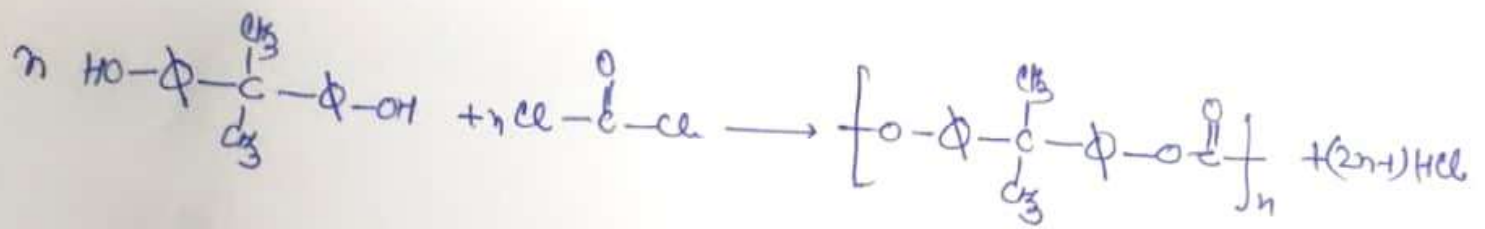
$$n \text{ HO-R-COOH} \rightarrow \text{H} \left[\text{OR}-\text{C}(=\text{O}) \right]_n \text{OH} + n \text{H}_2\text{O}$$

ARB

does not affect in presence of excess monomer as both the functional group concentration will increase.

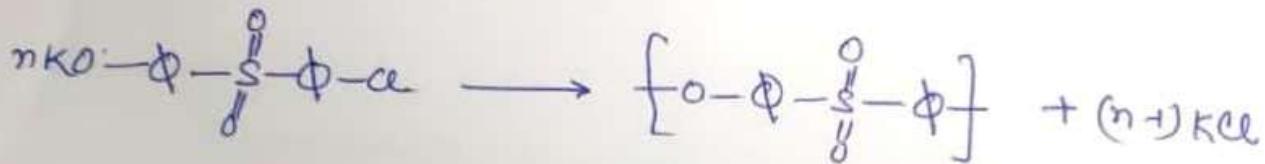


High Performance Aromatic Polymer Prepared by Polycondensation. (2)



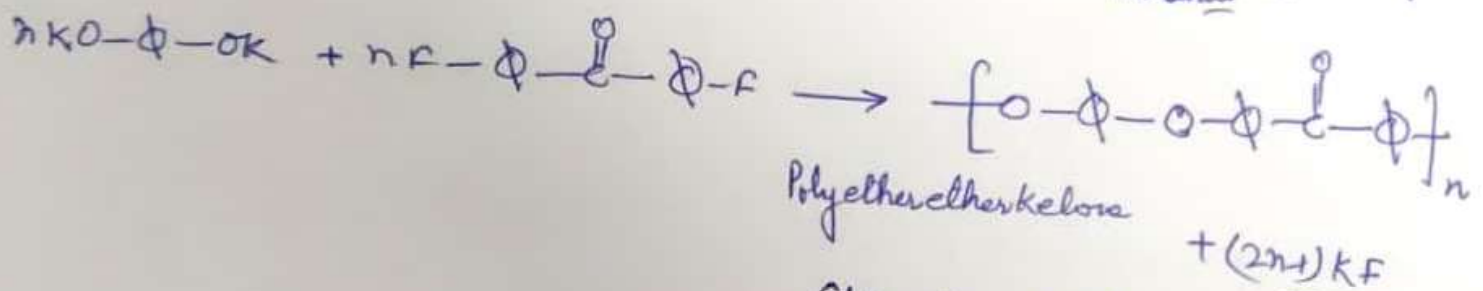
PolyCarbonate

Sheet, transparent and tough Screen.



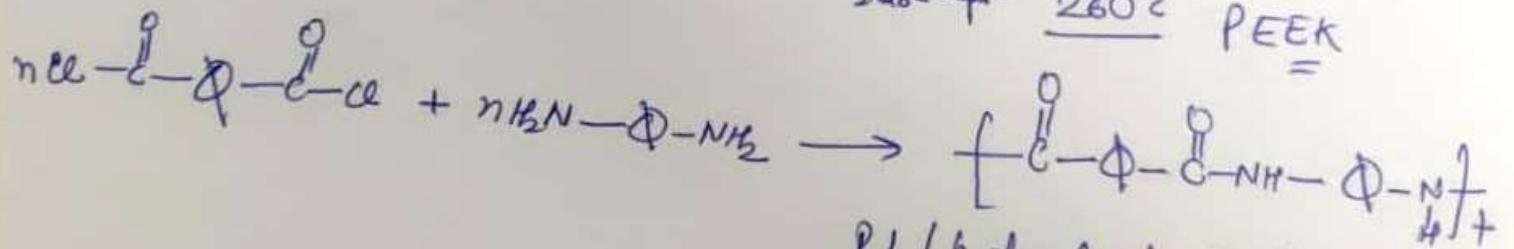
Polyether sulphone (PES)

Moulding, Coating
Membrane



Polyether ether ketone

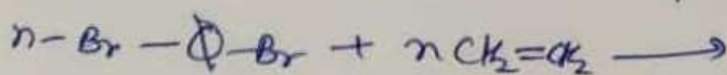
Stable up to 260°C PEEK



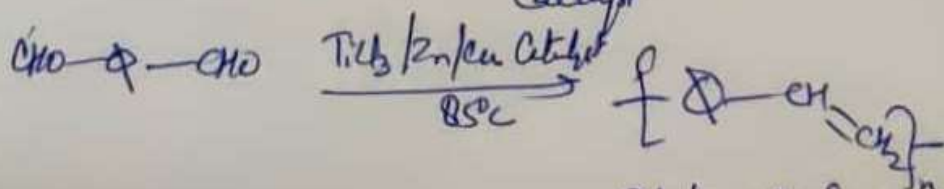
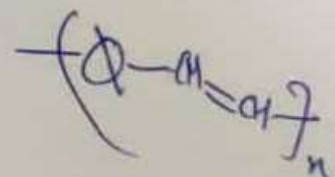
Poly(p-phenylene terephthalide)

Kevlar

$\text{RA}_2 + \text{RB}_2$ Polyaddition via Heck Coupling

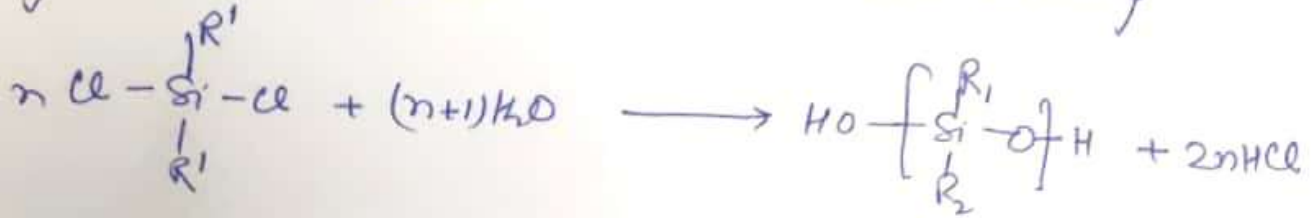


$\text{Pd}(\text{OCOMe})_2$ 100°C
Catalyst



Poly(3-Alkyl-2,5-thiophene)

Polysiloxanes: $-\text{Si}-\text{O}-$ excellent thermal stability related to 4(3)

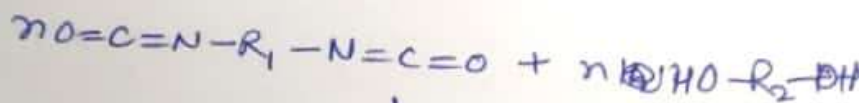


Polyaddition:

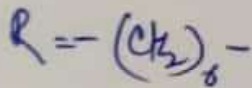
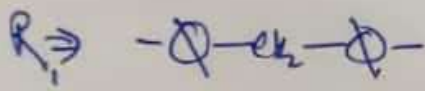
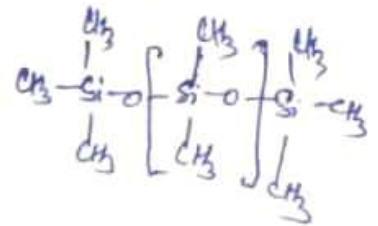
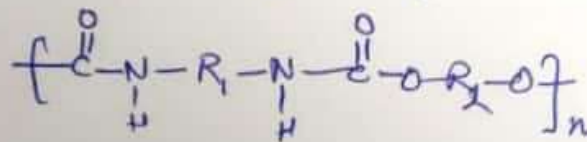
with removal of byproduct

$\text{R}_1 = \text{R}_2 = \text{CH}_3$
Poly(dimethyl siloxane)

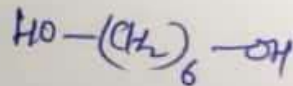
Linear Polyurethanes are prepared by $\text{RA}_2 + \text{RB}_2$ polyaddition of diisocyanates



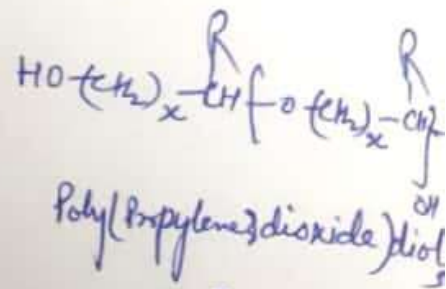
\downarrow at RT



Softness of Polyurethane is very much varying with changing Polyol,

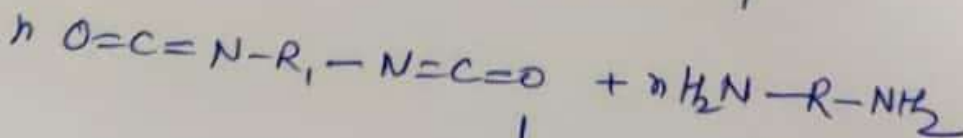


2, 3, 4, ...
rigid solid

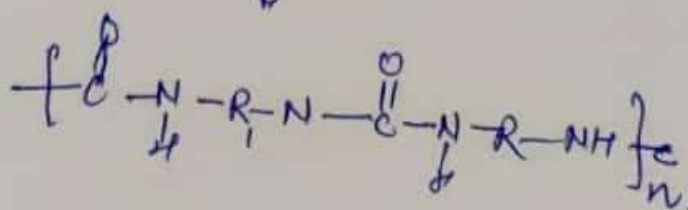


Poly(propylene)disoxide diol
2-8 kg/mol

diisocyanates with diamines yields polyureas.



\downarrow



Reaction rate is very fast

Carothers Theory predicts the growth of molecular weight (molar mass) during step growth polymerization and highlights that how number average degree of polymerization (\bar{x}_n) relates with monomer units

L1
P1

Hence $\bar{x}_n = \frac{N_0}{N} = \frac{\text{no. of monomer molecule present initially}}{\text{no. of monomer molecule remaining after time (t)}}$

Case 'A'

Consider equal reactivity theory (means equal no. of functional group available for polyⁿ by every monomer)

Hence, above \bar{x}_n can relate with extent of polymerization (p)

$$p = \frac{\text{no. of f}^{\text{nal}} \text{ group that reacted at } t}{\text{no. of f}^{\text{nal}} \text{ group present initially}}$$

Why f^{nal} group has been considered than N or N₀ - because monomer lose its identity even beginning of reaction, as they react and make dimer, trimer and so on...

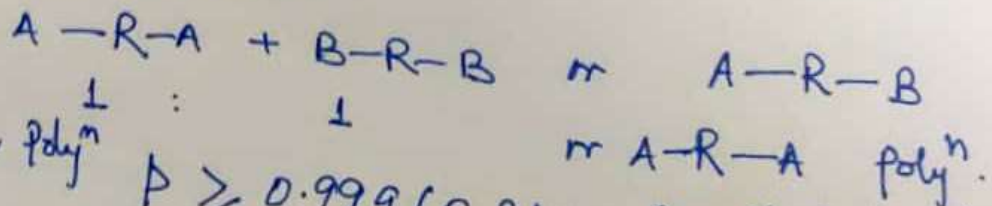
Hence, relating f^{nal} group instead of N make sense.

$$p = \frac{N_0 - N}{N_0} \Rightarrow p = 1 - \frac{N}{N_0} \Rightarrow \frac{N}{N_0} = 1 - p$$

$$= \frac{N_0}{N} = \frac{1}{1-p} = \bar{x}_n$$

$$\bar{x}_n = \frac{1}{1-p}$$

→ This is valid for f^{nal} group available in exact Stoichiometric balance like:



For any step growth polyⁿ

For example if

$$p \geq 0.999 \quad \bar{x}_n \quad (\text{for polymer of any physical use})$$

0.5	→	2
0.9	→	10
0.99	→	100
0.999	→	1000

Hence, purity of monomer is very important for step growth polyⁿ.

$$\bar{M}_n = \bar{M}_0 \cdot \bar{x}_n$$

Case B : Consider a step growth polyⁿ of RA_2 & RB_2

L1
P2

Hence in such case, ratio of functional groups present at $t=0$ are known or defined as Reactant Ratio (r)

at $t=0$ N_A \downarrow N_B
Present in excess

$$r = \frac{N_A}{N_B} \quad \text{it should be less than 1.}$$

at $t=0$ N_0
initial total f^{nal} group available for reaction

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

because each reactant has two f^{nal} group at $t=0$ but only one react with its counter monomer.

So at any time 't'

$$\frac{\text{no. of unreacted A group from } (RA_2)}{\text{no. of unreacted B group from } (RB_2)} = \frac{N_A - pN_A}{N_B - pN_A} \Rightarrow \frac{rN_B(1-p)}{N_B(1-rp)}$$

extent of reaction $\frac{1}{rN}$

Hence total f^{nal} group available at 't'

$$N = \frac{rN_B(1-p) + N_B(1-rp)}{2} = \frac{N_B(1+r-2rp)}{2}$$

General Carothers eq:

$$X_n = \frac{N_0}{N} = \frac{N_B(1+r)/2}{N_B(1+r-2rp)/2} = \frac{1+r}{1+r-2rp}$$

$$\text{if } p=1 \Rightarrow \boxed{X_n = \frac{1+r}{1-r}}$$

$$\text{if } r=1 \quad X_n = \frac{2}{1+1-2p} = \frac{1}{1-p}$$

Hence X_n can be related with p and r

based on the Comonomer taken \rightarrow it may be calculated even in presence of impurity: Consider a case where RA is present as impurity in $(RA_2 + RB_2)$ monomer system

Assignment: Please relate X_n, p, r for $(RA_2 + RB_2 + RA)$ system

How the Simple Statistical analysis can explain Flory have explained, the random nature of Step Growth Polymerization in order to predict the polymer size distribution

L1
P3

For example: we have $RA_2 + RB_2$ or ARB polyⁿ

We can find the probability $P(x)$ of existence of a molecule contains exactly x monomer repeat unit at time (t)

Hence $P(x) = (1-p) p^{(x-1)}$

1 group react $\rightarrow p$
2 $\rightarrow p^2$
3 $\rightarrow p^3$
 \vdots
 $(x-1) \rightarrow p^{x-1}$

finding a sequence of $(x-1)$ linkage
probability that last functional group is remain unreacted

Can be written in terms of Number of molecules present at time (t)

$$N_x = N(1-p)p^{x-1} \Rightarrow \text{we know } N = N_0(1-p)$$

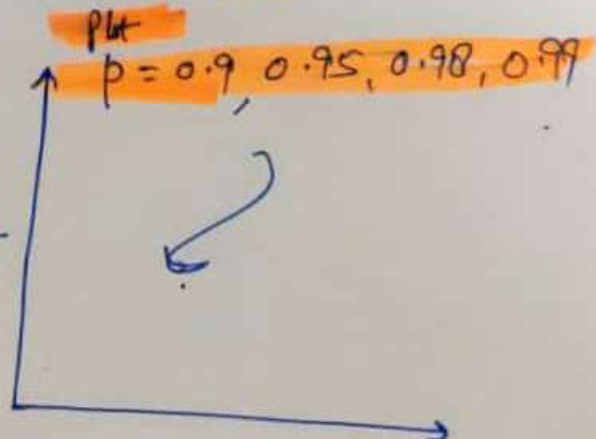
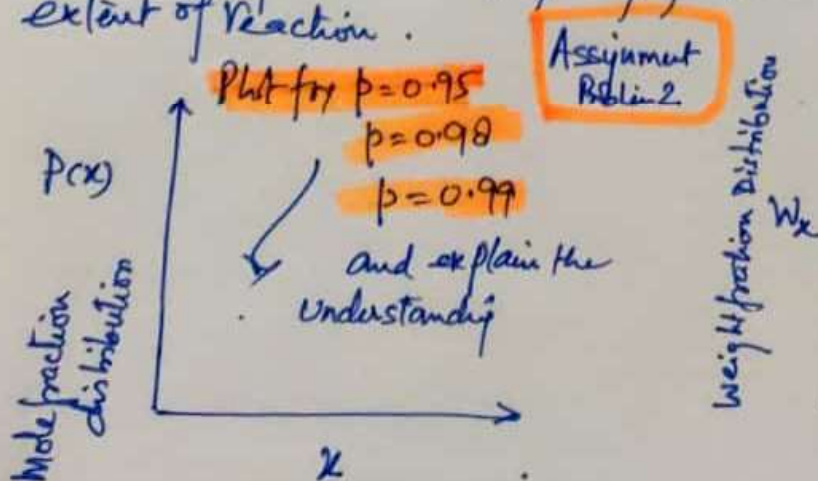
$$= N_0(1-p)^2 p^{(x-1)}$$

$$W_x = \frac{\text{Total mass of molecules with } D_n(x)}{\text{Total mass of all molecules}}$$

$$W_x = \frac{N_x(x\bar{M}_0)}{N_0\bar{M}_0} = \frac{x N_x}{N_0}$$

Hence $W_x = x(1-p)^2 p^{(x-1)}$

Define here the most probable distribution of molecules having weight fraction W_x is related to extent of reaction.



Contd...

no. of monomers in
mass of chain

Probability of molecules having x mer in chain

$$x=1$$

$$M_0$$

$$(1-p)$$

$$x=2$$

$$2M_0$$

$$p(1-p)$$

$$x=3$$

$$3M_0$$

$$p^2(1-p)$$

$$\vdots$$

$$x=i$$

$$iM_0$$

$$p^{i-1}(1-p)$$

$$\vdots$$

$$x=n$$

$$nM_0$$

We know $p(x) = (1-p)p^{i-1}$ $x=i$ $\frac{iM_0}{\sum iM_0} \sum (1-p)p^{i-1}$

$$\bar{M}_n = \sum x_i M_i = \sum iM_0(1-p)p^{i-1}$$

$$= M_0 \left[\sum i p^{i-1} - \sum i p^i \right]$$

We know $\sum i p^{i-1} = \frac{1}{(1-p)^2}$

Assignment: Solve Completely \Rightarrow

$$\bar{M}_n = \frac{\bar{M}_0}{1-p}$$

$$\bar{M}_w = M_0 \frac{(1+p)}{(1-p)}$$

weight average degree of $\Rightarrow (\bar{x}_w) = \frac{(1+p)}{(1-p)}$

$$\frac{\bar{M}_w}{\bar{M}_n} = 1+p$$

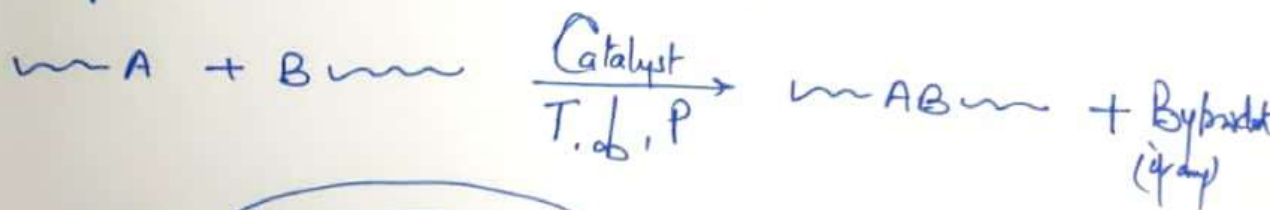
at $p \rightarrow 1$

$$\frac{\bar{M}_w}{\bar{M}_n} = 2 \text{ (PDI = 2)}$$

for step growth polymerization

L1
P5

Simple Reaction Kinetics: based on equal reactivity of functional group { Under this assumption, we will consider single rate constant for each step wise reaction.



$$-\frac{d[A]}{dt} = K' [A][B][Cat] = K_A C_B$$

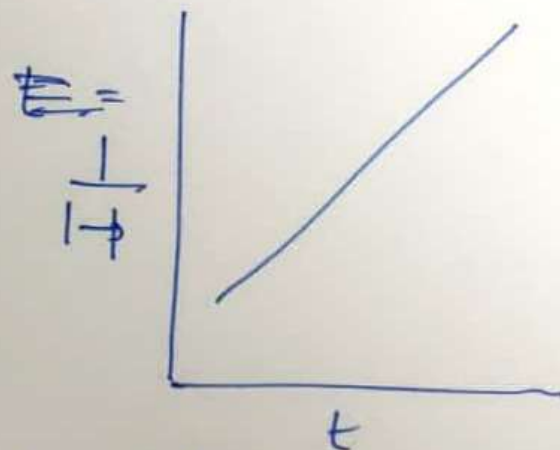
$$[A] = [B] = C_A = C_B = C$$

$$-\frac{dC}{dt} = KC^2 \Rightarrow -\int_0^C \frac{dC}{C^2} = \int_0^t K dt$$

$$\frac{1}{C} - \frac{1}{C_0} = Kt \quad \Leftrightarrow \quad \frac{C_0}{C} = \frac{N_0}{N}$$

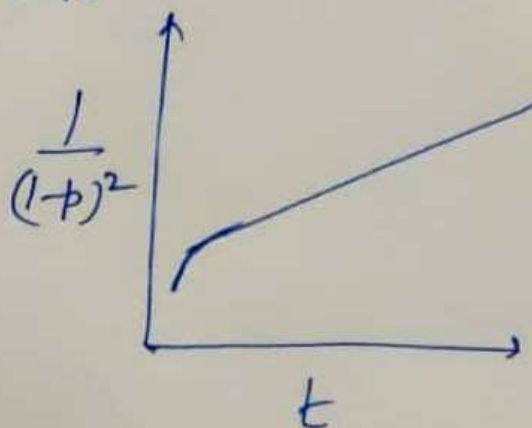
$$\boxed{\frac{1}{(1-p)} - 1 = C_0 Kt}$$

$y = mx$



if nit is not Catalysed

$$-\frac{dC}{dt} = K''C^3 \Rightarrow \frac{1}{(1-p)^2} = 1 + 2C_0^2 K''t$$



Assignment based on lectures 1:

1. Terephthalic acid is reacted with Ethylene glycol at equal molar concentration of 2 mol/lit. At what time from the start of polymerization have reached to 95% Conversion of Terephthalic acid. Consider the polyⁿ is of Self-Catalyzed in nature with rate Constant $k = 1.75 \times 10^{-2}$ lit/mol \cdot Sec. Also Calculate the molecular weight of PET as well.
2. Calculate the molecular weight of polybutylene isophthalate prepared from 1 mole 1,4 butane diol and 0.99 mole isophthalic acid when the polymerization reaction is terminated at 99.8%. What would be the maximum molecular weight if the reaction is not terminated at 99.8%.

Note: Please Submit AL1 by Monday 6, 2020 (12 Noon) by email.