

Gronariker.

P. 78

Kinetics of polymerization.



$$\text{rate} = kA^m B^n = -\frac{d[A]}{dt}$$

→ that is assuming differential as a molecular level rate law
→ k, m, n are experimentally determined

Introduction

Kinetics has a bearing on the speed of a reaction under a given set of conditions and on how these conditions will influence, among other things, the polymer molecular weight, molecular size, molecular weight distribution, chemical composition and indeed, the extent of polymer conversion.

Free-radical chain polymerization.

There are 3 steps - initiation, propagation and termination, in a polymerization reaction.

To initiate the reaction we need free radicals.



I is the initiator, \dot{R} the free radicals formed and k_d the initiator decomposition rate constant.

The rate of decomposition (R_d) of the initiator I is related to the concentration of the initiator ($[I]$) by the following equation: -

$$\frac{-d[I]}{dt} = R_d = 2k_d[I] \quad \text{②}$$

A factor of 2 is for a pair of radicals in ①

Rate of disappearance of monomer = $\frac{-dM}{dt} = k(\text{concentration})^n$ terms

Arrhenius eqn says that rate constant is related to T @

$$k_d = A e^{-E/RT} \quad (3)$$

A = frequency factor (constant)

E = activation energy

R = gas constant

T = temperature (Kelvin)

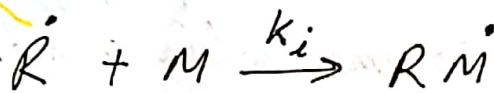
using (2) & (3)

$$R_d = 2k_d [I] = 2A e^{-E/RT} [I] \quad (4)$$

Rate of reaction = constant \times (concentration)ⁿ terms
or the rate of decomposition of an initiator

increases with temp. and concentration of the initiator

Free radical can attack monomer



↓
monomer

k_i = initiation rate constant

The rate of initiation \Rightarrow

$$-\frac{d[M]}{dt} = R_i = k_i [R] [M] \quad (6)$$

↑
Rate of initiation

Free radicals have such a high reactivity that they attack the monomer immediately after decomposition of the initiator.

\therefore rate of formation should be = rate of disappearance
or $R_i = R_d$

$$R_i = 2k_d [I] \quad (7)$$

This is true ~~iff~~ if all the free radicals produced

~~that~~ are effective in initiating the polymer growth.

Actually, some of them are not effective side products due to other processes such as recombination.

f = fraction of effective free radicals effective in initiating chain growth.

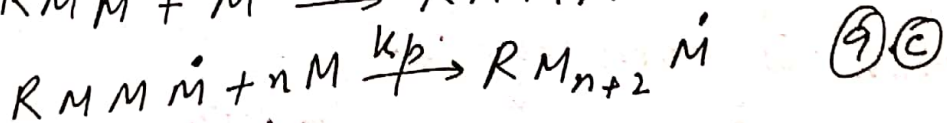
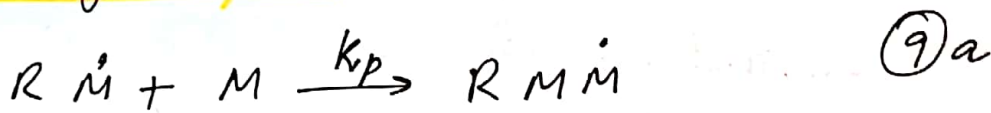
$$R_i = 2f k_d [I] \quad (8)$$

f lies between 0.6 & 1.0.

f gives the efficiency of the initiator.

0.6 means $\left\{ \begin{array}{l} 60\% \text{ of effective free radicals} \\ 40\% \text{ loss as side products} \end{array} \right.$

Propagation follows initiation:-



where k_p is the propagation rate constant.

Rate of propagation (R_p) is represented by

$$\frac{-d[M]}{dt} = R_p = k_p [\dot{M}] [M] \quad (10)$$

for $\dot{M} + M \rightarrow M \dot{M}$

or

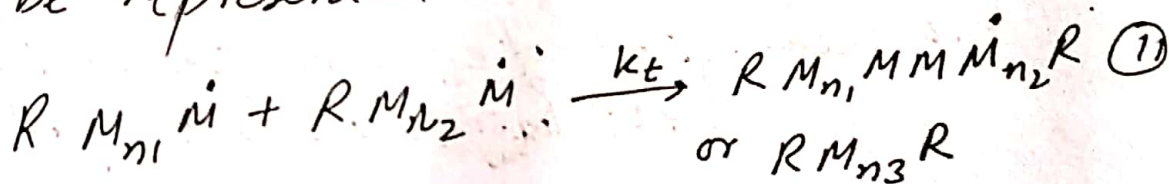
Propagation rate is $\propto [M^{\cdot}]$ & $[M]$

$[M^{\cdot}]$ = concentration of ^{reactive} free radical sites
(i.e. concentration of growing chains)

$[M]$ = concentration of the monomer.

The final step is in termination.

If it occurs by coupling or combination of two growing chains (i.e. coupling); it can be represented as



where k_t is the termination rate constant.

The corresponding rate eqn for the termination process is given by :-

$$-\frac{d[M^{\cdot}]}{dt} = R_t = 2k_t[M^{\cdot}]^2 \quad (12)$$

for $M^{\cdot} + M^{\cdot} \rightarrow MM^{\cdot}$
↳ two chains are combined

~~when~~ number of chain growths initiated equals the number of chain growths arrested = steady state.

At steady state, $R_i = R_t$ (13)

From (8) & (12) $2k_d f [I] = 2k_t [M^{\cdot}]^2$

$$[\dot{M}]^2 = \frac{k_d f [I]}{k_t}$$

$$[\dot{M}] = \sqrt{\frac{k_d f [I]}{k_t}} \quad (14)$$

From (10) we have $[\dot{M}] = \frac{R_p}{k_p [M]}$ (15)

On substituting $[\dot{M}]$ in (14)

$$\frac{R_p}{k_p [M]} = \sqrt{\frac{k_d f [I]}{k_t}}$$

$$R_p = k_p \sqrt{\frac{k_d}{k_t}} (f [I])^{1/2} [M] \quad (16)$$

$$R_p \propto [M][I]^{1/2}$$

Rate of polymer formation is \propto the 1st power of the monomer concentration and also to the $\sqrt{}$ of the initiator concentration.

Equation for kinetic chain length (\bar{v})

\bar{v} = average number of monomer molecules consumed by each effective free-radical generated by the initiator. ~~It is the~~

It expresses the number of monomer molecules added to a growing chain from its initiation upto

termination.

$$v = \frac{\text{rate of propagation}}{\text{rate of initiation}} = \frac{\text{rate of propagation}}{\text{rate of termination}}$$

$$= \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad (17)$$

Using (16) & (8) in (17)

$$\frac{R_p}{R_i} = \frac{k_p \sqrt{\frac{k_d}{k_t}} \sqrt{f} \sqrt{[I]} [M]}{2f k_d [I]}$$

$$v = \frac{k_p [M]}{\sqrt{k_d k_t f} [I]} \quad (18)$$

$$v \propto \frac{[M]}{\sqrt{[I]}}$$

Degree of polymerization.

As the kinetic chain length gives the number of monomer molecules present in a growing chain at the time of termination, \bar{D}_p can be correlated as follows :-

① $\bar{D}_p = 2v$, when termination occurs by coupling.

② $\bar{D}_p = v$, when " occurs by disproportionation.

and
 (3) $\bar{D}_p = \frac{v_p}{N}$ where N has a value of 0.5 for termination by coupling and 1 for termination by disproportionation.

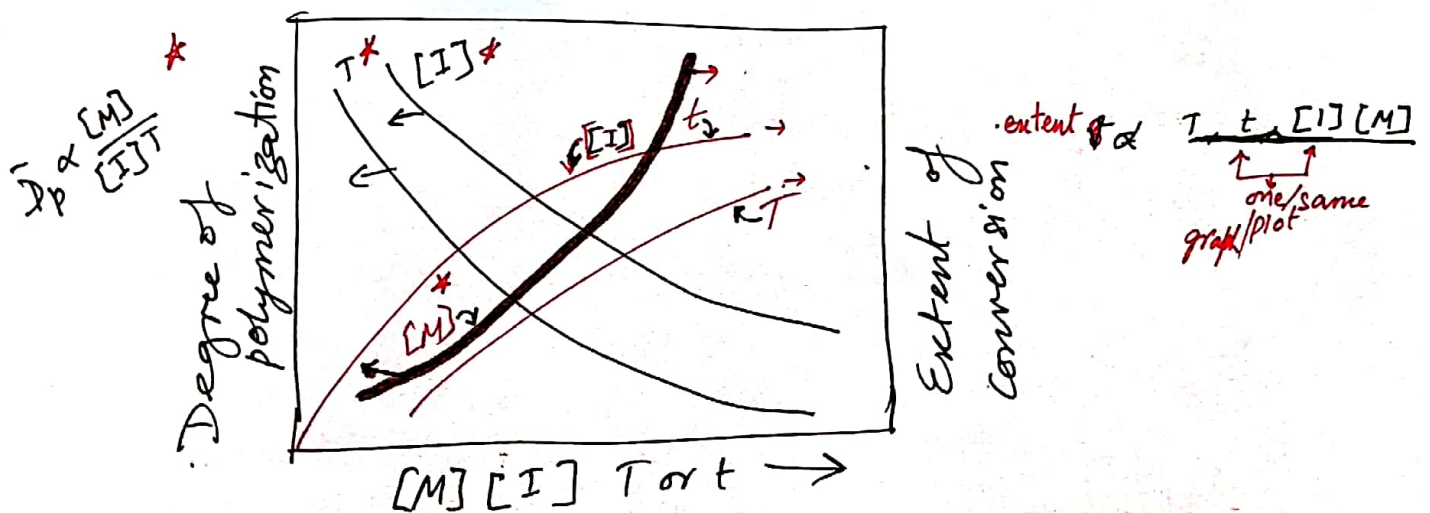
or

$$\bar{D}_p \propto \frac{[M]}{\sqrt{[I]}}$$

Generalised Statement regarding radical polymerization.

(a) The degree of polymerization decreases with an increase of temperature and of initiator concentration and with a decrease of monomer concentration.

(b) The extent of conversion (i.e. the amount of monomer converted into polymer) increases with an increase of (i) temperature (ii) polymerization time & (iii) initiator and monomer concentrations.

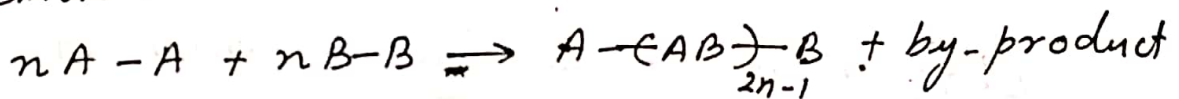


Polycondensation

Assumptions proposed by Flory :-

So long as the molecules are not quite small, the intrinsic reactivity of the functional groups present in them are independent of the molecular size.

Similarly, the effect of viscosity of the reaction medium and factors such as diffusion rate contribute ~~to~~ negligibly to the overall kinetics of a condensation reaction.



Non catalyzed polycondensation

Take • the synthesis of a polyester from a dicarboxylic acid and a diol. Presently, the esterification reaction is not catalyzed by acids. Hence dicarboxylic acid acts as a reactant and a catalyst.
(2 hydroxyl grp)

Hence the reaction rate will be proportional to the square of the concentration of the carboxylic acid group and to the first power of the hydroxyl group concentration.

$$\frac{-d[\text{COH}]}{dt} = k [\text{COOH}]^2 [\text{OH}]$$

(47)

k = esterification rate constant.

When $[OH] = [COOH] = [FG]$ at given time t .
 i.e., when we take stoichiometric quantities
 of the functional groups or conc. of $-OH = \text{conc. of } -COOH$

$$-\frac{d[FG]}{dt} = k [FG]^2 [FG] = k [FG]^3 \quad (48)$$

Integrating we have

$$2kt = \frac{1}{[FG]^2} - \frac{1}{[FG]_0^2} \quad (49)$$

$[FG]_0$ represents the initial concentration of $-COOH$ or $-OH$. If p represents the fraction of the functional groups which has undergone the esterification reaction (i.e., the extent of reaction) at a time t , then $[FG]$ could be related to $[FG]_0$ using

$$\frac{[FG]_0 - [FG]}{[FG]_0} = p \quad (50a)$$

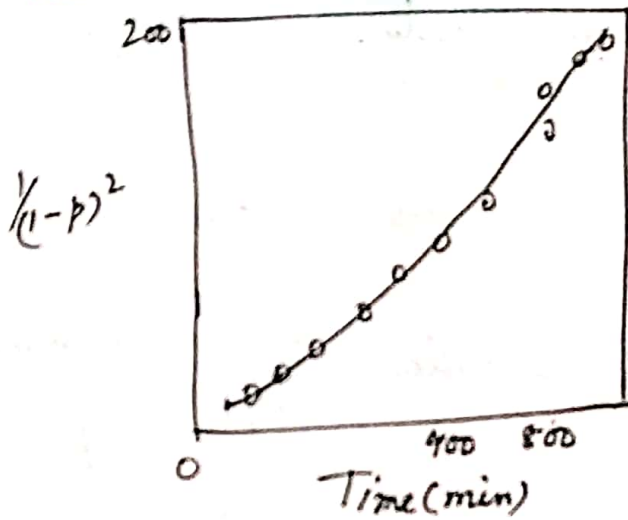
$$\frac{[FG]}{[FG]_0} = 1 - p \quad (50b)$$

$$[FG] = [FG]_0 (1 - p) \quad (51)$$

Using (49) \bullet $2kt = \frac{1}{[FG]_0^2 (1-p)^2} - \frac{1}{[FG]_0^2} \quad (52)$

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

(52)



plot showing reaction kinetics for condensation of adipic acid with diethylene glycol (in absence of any added catalyst) at 166°C.

(52) This implies that a graphical plot of $\frac{1}{(1-p)^2}$ must be linear.

Consider a simple esterification reaction, which proceeds without any side reaction.

The number average degree of polymerization \bar{D}_{pn} may be related to p , the fraction of the functional groups which has undergone the esterification at a time t , by -

$$\bar{D}_{pn} = \frac{1}{(1-p)} = \frac{[FG]_0}{[FG]}$$

(53)

$$\bar{D}_{pn}^2 = \frac{1}{(1-p)^2} = \frac{[FG]_0^2}{[FG]^2} = 1 + 2kt[FG]_0^2$$

or

$$\bar{D}_{pn}^2 = 2k_p [F-G]_0^2 t + 1$$

(54)

~~\bar{D}_{pn}^2 appears as~~ \bar{D}_{pn}^2 appears as 2nd power & time as first power. Hence polymer molecular weight will increase only slowly. ~~$\bar{D}_{pn} \propto \sqrt{t}$~~

Extent of reaction & degree of polymerization

p	(%) extent of conversion	Degree of polymerization $\bar{D}_{pn} = \frac{1}{1-p}$
-----	--------------------------	--

0.50	50	2
0.9	90	10
0.95	95	20
0.99	99	100
0.999	99.9	1,000
0.99999	99.999	100,000

Effect of extent of conversion on degree of polymerization for polycondensation reaction.

Acid catalyzed polycondensation

Condensation reactions are enhanced by the presence of strong acids. governing eqn =

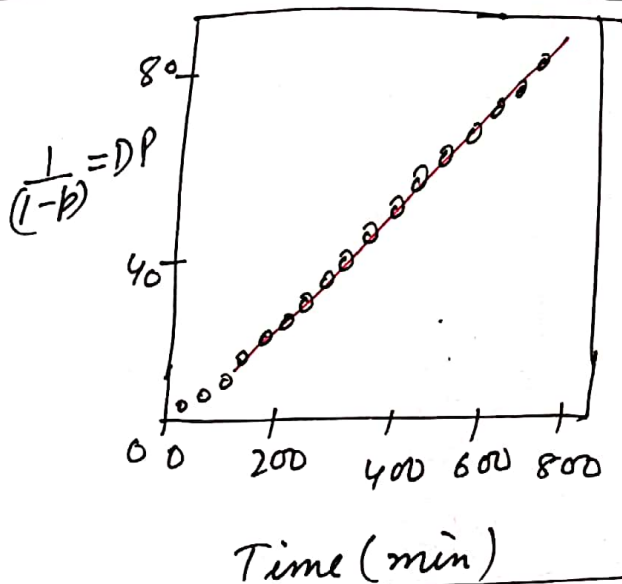
$$-\frac{d[FG]}{dt} = k_x [\text{COOH}][\text{OH}] = k_x [FG]^2 \quad (55)$$

Integ. $\frac{1}{[FG]} - \frac{1}{[FG]_0} = k_x t$

$k_x = k[X]$; $[X]$ is the concentration of the catalyst. $[FG] = [FG]_0(1-p)$

$[X]$ remains same throughout the reaction.

$$k_x [FG]_0 t = \frac{1}{(1-p)} - 1 \quad (56)$$



Plot showing reaction kinetics for the condensation of adipic acid with diethylene glycol at 109°C. (Catalyzed by 0.4 mole% of toluene sulphonic acid)

Similarly this eqn can be derived

$$\bar{D}_{pn} = k_x [FG]_0 t + 1 \quad (57)$$

indicating that the molecular weight built up in this case will be faster than in the polycondensation reaction without acid catalyst.

~~$\bar{D}_{pn} \propto t$~~