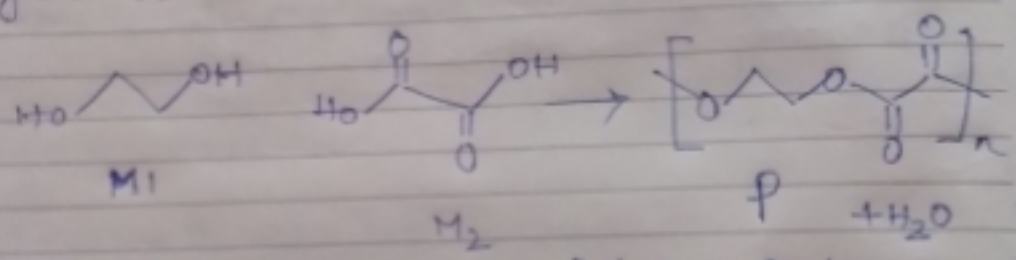


Kinetics of Step growth Polymerization.

It is important to understand how reactions proceed over time. This information can tell us how long it will take for a polymer to reach an optimum length. It provides insight into how the polymerization occurs.

Condensation Polymers grow through a step growth process. Example: Formation of Polyesters.



We expect every time a polymer molecule is made, a monomer molecule is used up.

$$\text{Rate} = \frac{d[\text{P}]}{dt} = -\frac{d[\text{M}_1]}{dt} = -\frac{d[\text{M}_2]}{dt}$$

$$\text{Rate} = k[\text{M}_1][\text{M}_2]$$

but if $[\text{M}_1] = [\text{M}_2] = [\text{M}]$, then $\text{Rate} = k[\text{M}]^2$
 So we have here is a simple second-order reaction.

$$\text{Rate} = -\frac{d[\text{M}]}{dt} = k[\text{M}]^2$$

$$-\frac{d[\text{M}]}{[\text{M}]^2} = k t$$

Integrating:

$$\int_{[M]_0}^{[M]} \frac{-d[M]}{[M]^2} = \int_{t=0}^t k dt$$

$$\frac{1}{[M]} - \frac{1}{[M]_0} = kt$$

If we were to measure monomer concentration periodically during the polymerization and plot its inverse over time, we would obtain a straight line. The slope of the line would be the rate constant, and the intercept would reflect the inverse of the monomer concentration with which we had started the reaction.

At this point we need to pause and talk about what we actually mean by monomer concentration.

$$[OH] = [CO_2H] = 16$$

$$[CO_2R] = 0$$

$$DP_n = 0$$

$$[OH] = [CO_2H] = 8$$

$$[CO_2R] = 8$$

$$DP_n = 2$$

In step-growth polymerization, the majority molecules are probably reacting at roughly similar rates. Two monomers link to give dimer, two dimers form tetramers, two tetramers form octamers and so on. Nobody is really interested in how quickly monomers turn into dimers. ~~They~~ we want to know the growth of the polymer chain in progressing.

02

FRIDAY

AUGUST

214-151 • WK 31

1	2	3	4	5	6	7	8	9	10	11	12	13	14	J
15	16	17	18	19	20	21	22	23	24	25	26	27	28	U
29	30	31												L
W	T	F	S	S	M	T	W	F	S	S				

After all, once the monomers are gone, the same esterification reaction keeps happening and it's really the concentration of alcohols and carboxylic acid groups matter, whether they are found in dimers, tetramers etc. Average degree of polymerization increases

10 Degree of polymerization $DP_n = \bar{X}_n = \frac{[M]_0}{[M]}$

11 $[M] \rightarrow$ Concentration of reactive functional group in those monomer.

12 Fraction of monomer remaining = $\frac{[M]}{[M]_0}$

2 Fraction monomer converted to ester $p = 1 - \frac{[M]}{[M]_0}$

3 or $1 - p = \frac{[M]}{[M]_0}$

4 or $\frac{1}{1-p} = \frac{[M]_0}{[M]}$ or $\boxed{\bar{X}_n = \frac{1}{1-p}}$

5 Now look at them in the context of our second order kinetics

6 $\frac{1}{[M]} - \frac{1}{[M]_0} = kt$

multiplied both side by $[M]_0$

$\frac{[M]_0}{[M]} - \frac{[M]_0}{[M]_0} = [M]_0 kt \quad \text{--- (i)}$

$$DP_n = \bar{X}_n = \frac{[M]_0}{[M]}$$

$$\text{or } \frac{[M]_0}{[M]} - 1 = [M]_0 k t$$

$$\text{but } p = 1 - \frac{[M]}{[M]_0}$$

$$\boxed{\frac{1}{1-p} = \frac{[M]_0}{[M]}}$$

Substituting this value in eqn. (i)

$$\frac{1}{1-p} - 1 = [M]_0 k t$$

$$\text{or } \boxed{DP_n = \bar{X}_n = \frac{[M]_0}{[M]}}$$

Substituting this in eqn. (1) we get

$$X_n - 1 = [M]_0 k t$$

This relation indicates the
 w degree of polymerization
 increase linearly over time.

05

MONDAY

AUGUST

217-148 • WK 32

1	2	3	4	5	6	7	8	9	10	11	12	13	14
15	16	17	18	19	20	21	22	23	24	25	26	27	28
29	30	31											
M	T	W	T	F	S	S	M	T	W	T	F	S	S

19

Mechanism and Kinetics of radical Chain Polymerization

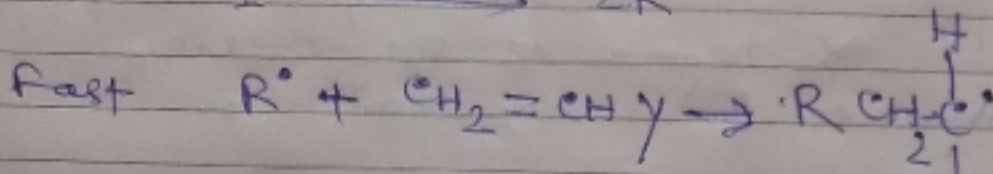
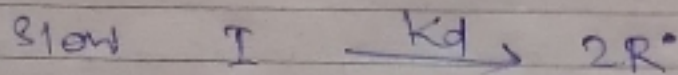
Introduction: * Polymerization is possible if $\Delta G < 0$ for the transformation of monomers to polymer. This will depend only on initial and final states not the nature of intermediate.

* Substituents on a vinyl group will influence reactivity through inductive, resonance and steric effect.

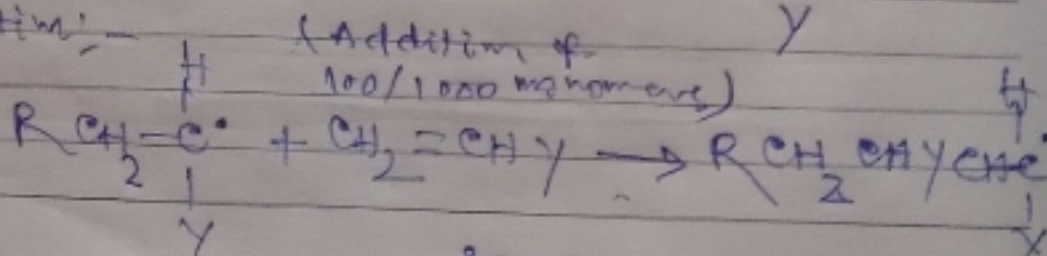
* radicals are free species, but anionic and cationic end groups have counterions that influence reactivity.

* In a chain reaction, increasing the reaction time simply increases the amount of high polymer produced.

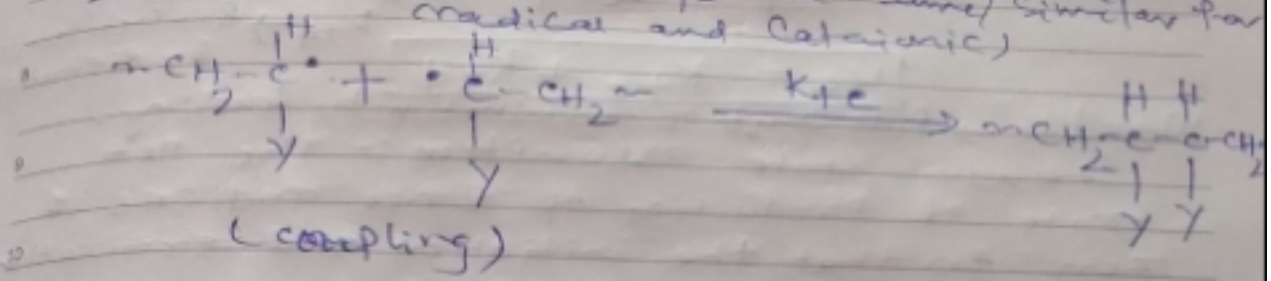
Mechanism: (Thermal or photochemical bond cleavage)



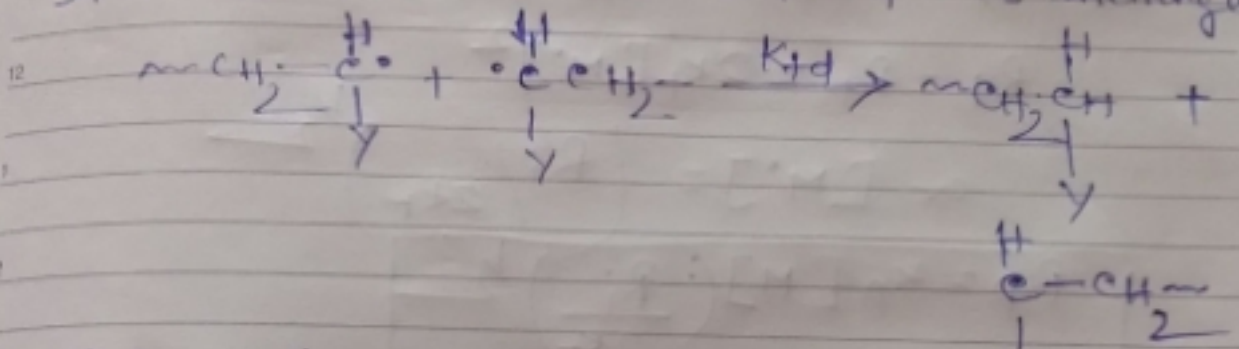
Propagation:



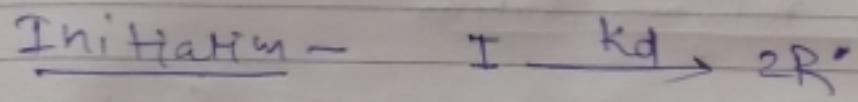
10 Termination (Reactions are same/similar for radical and Cationic)



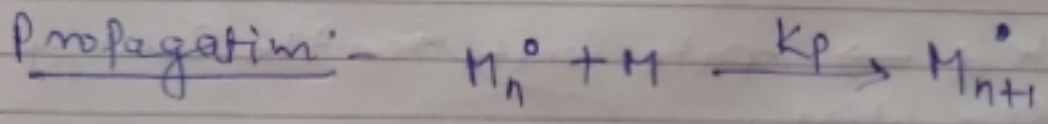
11 Disproportionation (molecular k_t is unchanged)



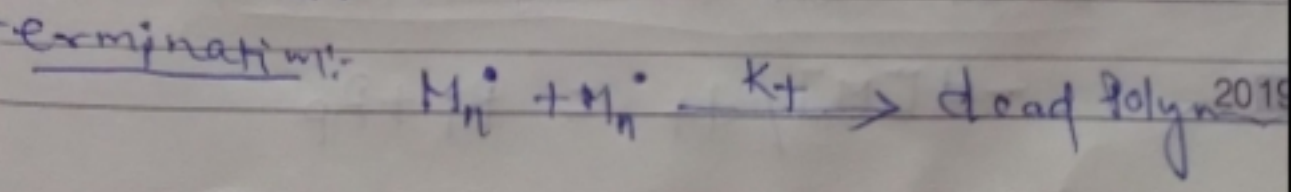
Most anionic reactions have no inherent termination step.



rate = $-\frac{d[\text{I}]}{dt} = R_i = k_d[\text{I}]$



$-\frac{d[\text{M}]}{dt} = R_p = k_p[\text{M}^\bullet][\text{M}]$



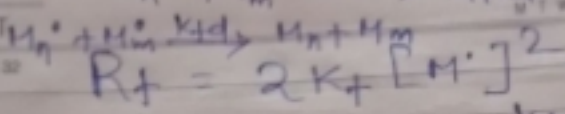
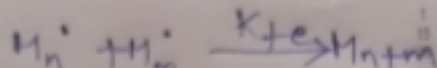
The two different termination

07

WEDNESDAY

AUGUST

219-140 • WK 32



$$R_t = 2k_t [M^\bullet]^2$$

$k_{td} \rightarrow$ Rate const. termin. by disproportionation

$$k_t = k_{te} + k_{td}$$

- When k_{td} is large, rate const. of termination by coupling.
- Steady-state assumption: The net rate of production of free radicals is zero so that the initiation and termination rates are equal. This is usually true after t_{min} reaction.

$$R_i = R_t = 2k_t [M^\bullet]^2$$

$$\text{or } [M^\bullet] = \left(\frac{R_i}{2k_t} \right)^{1/2}$$

$$R_p = k_p [M] \left(\frac{R_i}{2k_t} \right)^{1/2}$$

Kinetics of Free radical Chain Polymerization

Radical chain polymerization sequence

- of three steps: initiation, propagation & termination

$k_d \rightarrow$ rate const. for the catalyst dissociation

The rate of monomer disappearance is called rate of polymerisation

$$-d[M]/dt = R_i + R_p$$

$$R_p = k_p [M] (R_i / 2k_t)^{1/2}$$

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

Average kinetic chain length \bar{n} which is defined as the average no. of monomer units polymerized per chain initiated, which is equal to the rate of polymerisation $R_p = R_t$ under steady state condition.

$$\bar{n} = \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad \text{--- (ii)}$$

Substituting R_i and R_t in equⁿ (ii)

$$\bar{n} = \frac{k_p [M] [M^*]}{2k_t [M^*]^2} = \frac{k_p [M]}{2k_t [M^*]} \quad \text{--- (iii)}$$

Substituting $[M^*]$ in equⁿ (iii) we get

$$\bar{n} = \frac{k_p [M]}{2(f k_d k_t [I])^{1/2}}$$

Kinetic chain length is related to a variety of rate and concentration parameters. Thus varying initiator concentration can control molecular weight.

kinetic ~~had~~ chain length is related to directly to degree of polymerisation. 2019