POLYMERIZATION KINETICS

THERMODYNAMICS

Tells us where the system would like to go eventually *!! ie.defines relationships between macroscopic variables at equilibrium*

KINETICS

Tells us how fast *the system takes various reaction paths*

EXAMPLES

SUGAR + OXYGEN $\longrightarrow$ PRODUCTS + ENERGY

CRYSTALLIZATION IS ALSO A PROCESS CONTROLLED BY KINETICS, AS WE WILL SEE LATER

POLYMERIZATION KINETICS

STEP GROWTH -   SLOW

Can use statistical methods
as well as kinetics to describe
mol. wt. distributions – more
on this later

CHAIN Polymerization   –   FAST

Can apply statistical methods
to an analysis of the
microstructure of the products,
but not the polymerization
process and things like mol .wt.

KINETICS OF STEP GROWTH POLYMERIZATION

WHY BOTHER ?

- *How long does it take to make polymer ?*

- *Can we speed up the reaction ?*

- *What is the relationship between kinetics and the Mol. Wt. Of the product ?*

REVISION

RATE OF REACTION $=$ CONSTANT x $[\text{CONCENTRATION}]^n$ TERMS

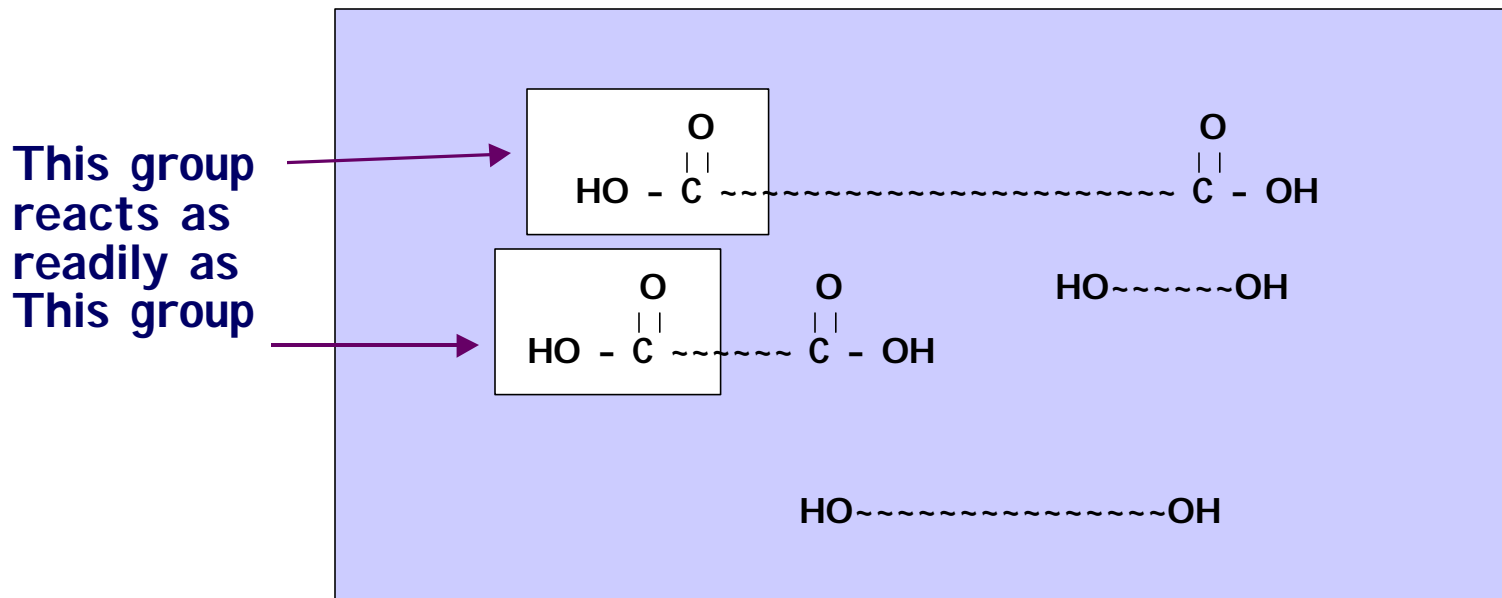RATE OF DISAPPEARANCE OF MONOMER $= -\dfrac{dM}{dt}$

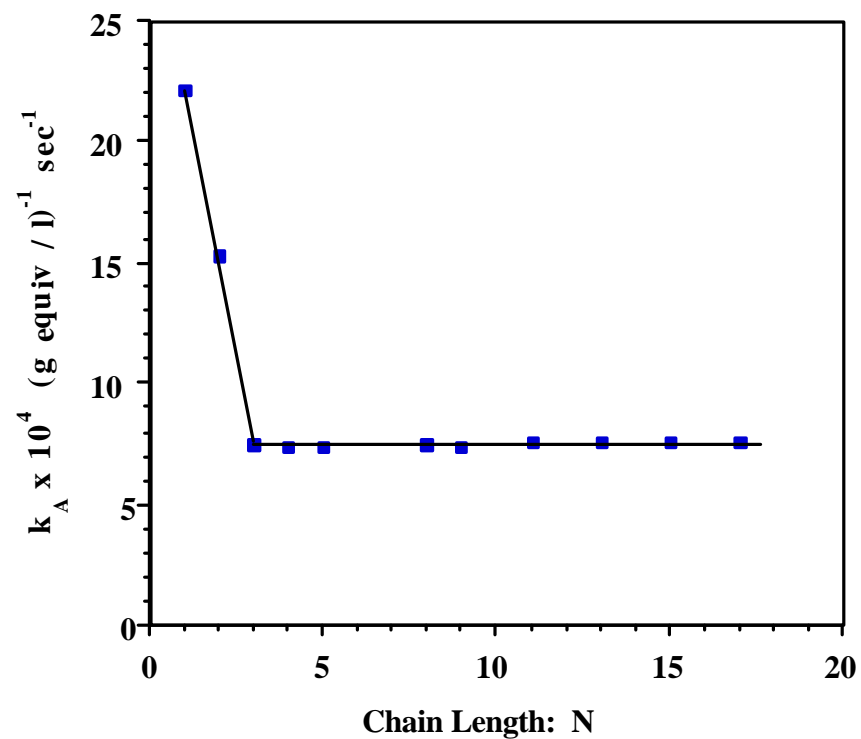$= k \times [\text{CONCENTRATION}]^n$ TERMS

KINETICS OF POLYCONDENSATION

KEY ASSUMPTION – FLORY

The reactivity of a functional group is independent of the length of the chain to which it is attached

EXAMPLE:

DIBASIC ACID + GLYCOL $\longrightarrow$ **POLYESTER**

WAS FLORY RIGHT?

Redrawn from the data of Flory,P.J.,
Principles of Polymer Chemistry,Cornell
University Press, 1953, p71

KINETICS OF POLYCONDENSATION

A – A + B – B $\longrightarrow$ A– AB – B

Kinetic equation for this type of reaction is usually of the form:

$$\text{Reaction Rate} \;=\; -\frac{d[A]}{dt} \;=\; k_2[A][B]$$

N.B. [A] AND [B] ARE THE CONCENTRATIONS OF *FUNCTIONAL GROUPS*

However, esterifications are acid catalyzed and *in the absence of added strong acid*

$$-\frac{d[A]}{dt} \;=\; k_3[A]^2[B]$$

MORE KINETICS

$$-\frac{d[A]}{dt} = k_3 [A]^2 [B]$$

If [A] = [B]

$$c = [A] = [B]$$

Hence

$$-\frac{dc}{dt} = k_3\, c^3$$

$$\int_{c_o}^{c} \frac{dc}{c^3} = k_3 \int_{t=0}^{t} dt$$

$$2\,k_3\, t = \frac{1}{c^2} - \frac{1}{c_o^2}$$

EXTENT OF REACTION

Define

$$p = \text{EXTENT OF REACTION}$$

In this example

$$\text{LET } p = \frac{\text{\# OF COOH GROUPS REACTED}}{\text{\# OF COOH GROUPS ORIGINALLY PRESENT}}$$
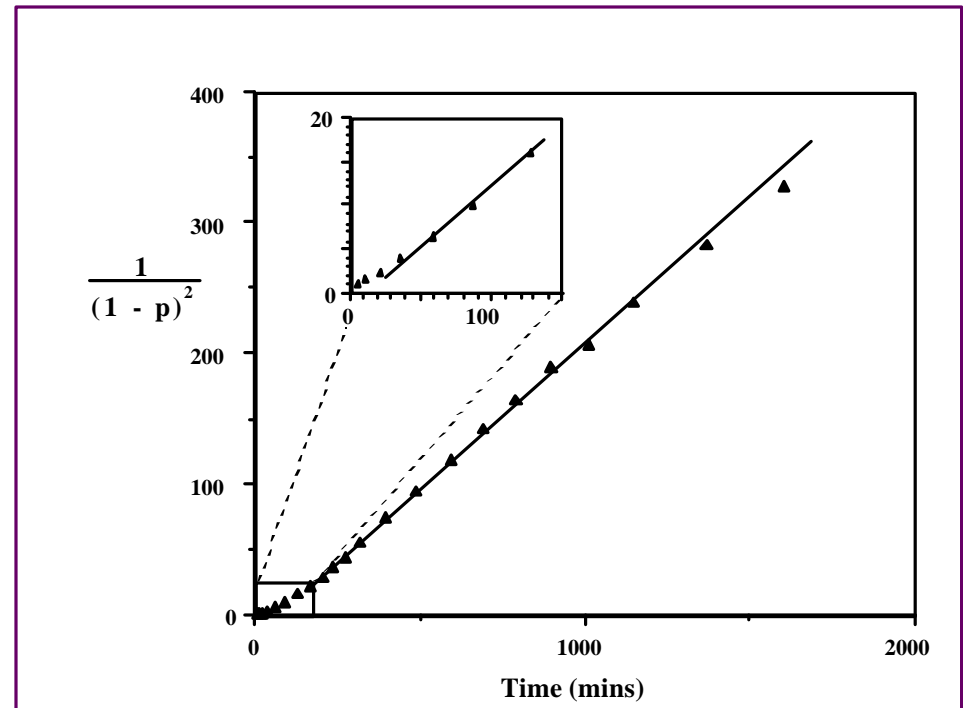
Then

$$c = c_0 (1-p)$$

And

$$2 c_0^2 k_3 t = \frac{1}{(1-p)^2} - 1$$

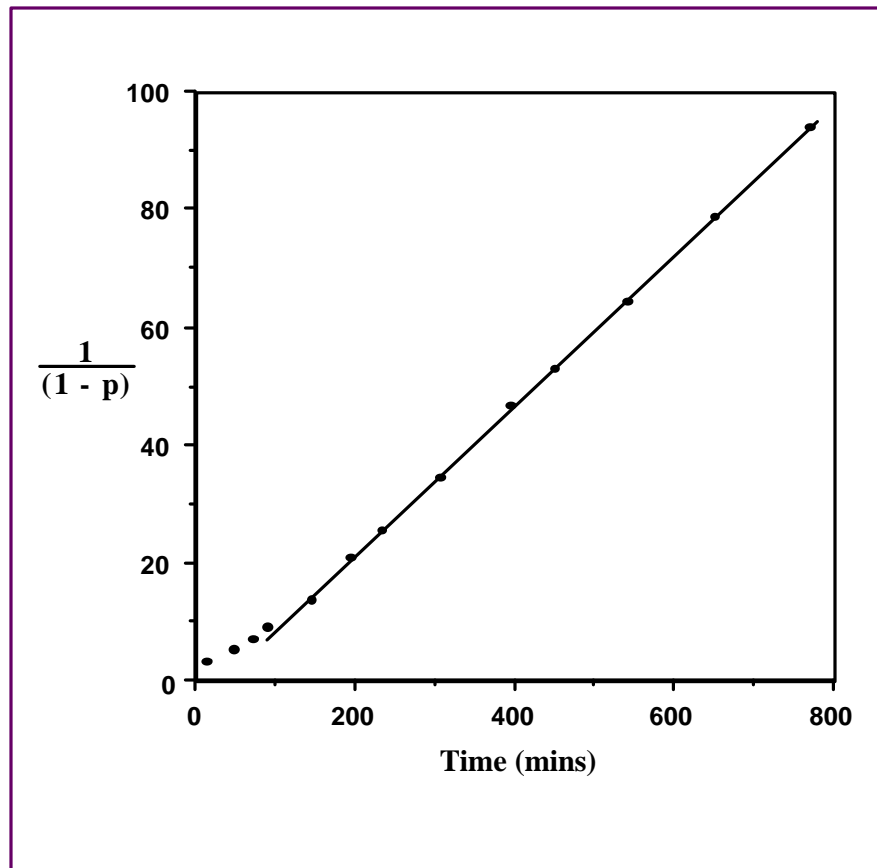Redrawn from the data of Flory, P.J., J.A.C.S., 61, 3334 (1939)

ACID CATALYZED REACTION

$$-\frac{d\,[COOH\,]}{dt} = k'\,[COOH\,]\,[OH\,]$$

$$-\frac{dc}{dt} = k'c^2$$

$$c_0\,k'\,t = \frac{1}{(1-p)} + constant$$

Note; the concentration of the acid
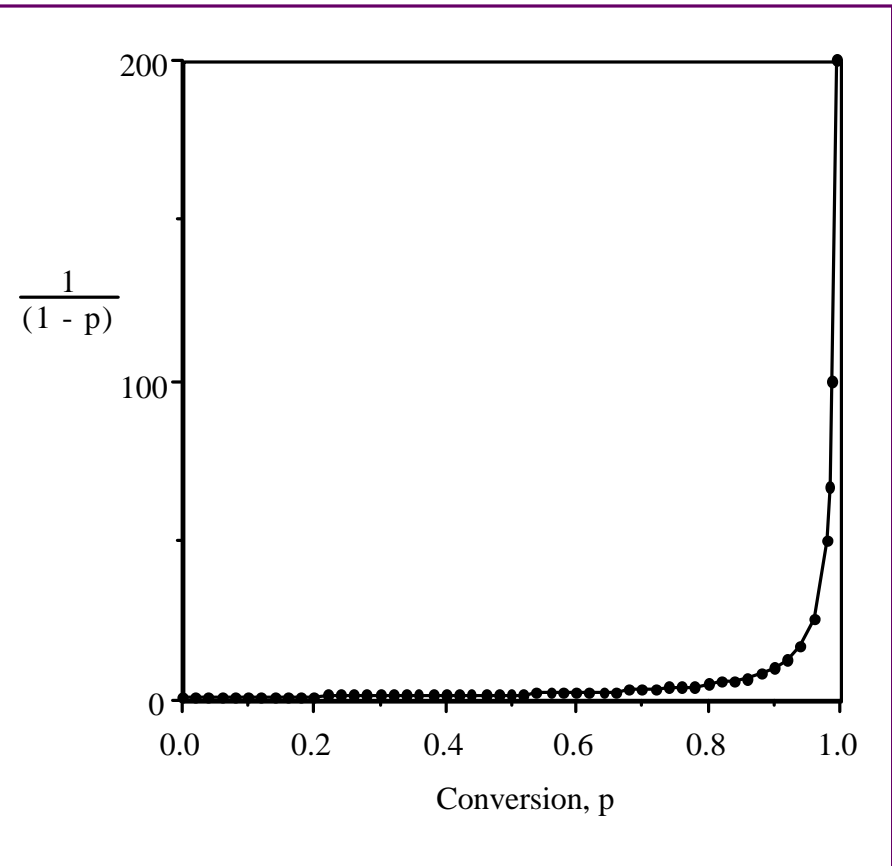*catalyst (a constant) is included in k'*

NUMBER AVERAGE DEGREE
OF POLYMERIZATION

$$\overline{x}_n = \frac{N_0}{N}$$

$$= \frac{c_0}{c} = \frac{c_0}{c_0(1-p)}$$

ie $\quad \overline{x}_n = \dfrac{1}{(1-p)}$
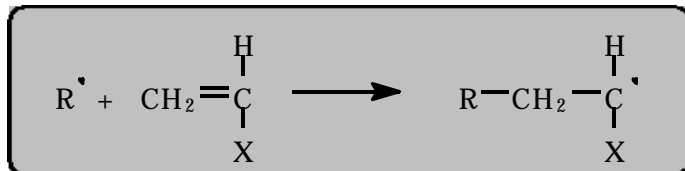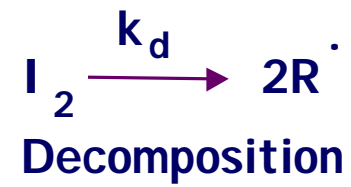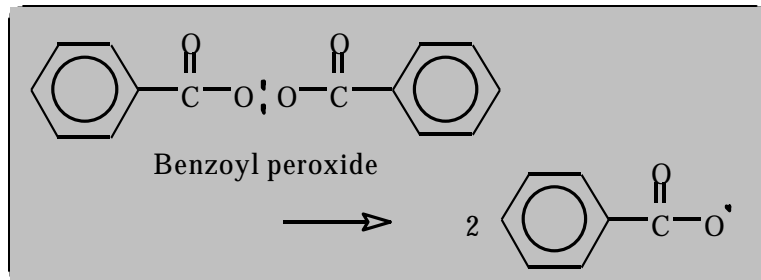
$$\overline{M}_n = M_0 \overline{x}_n = \frac{M_0}{(1-p)}$$
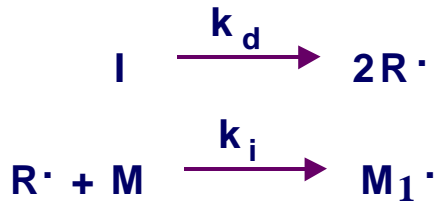
KINETICS OF FREE RADICAL POLYMERIZATION

We need to consider the following steps

- INITIATION

- PROPAGATION

- (CHAIN TRANSFER)

- TERMINATION

INITIATION

Benzoyl peroxide

$$I_2 \xrightarrow{k_d} 2R\cdot$$

Decomposition

$$R\cdot + M \xrightarrow{k_i} M_1\cdot$$

Addition

INITIATION

$$I \xrightarrow{\text{k}_d} 2R \cdot$$

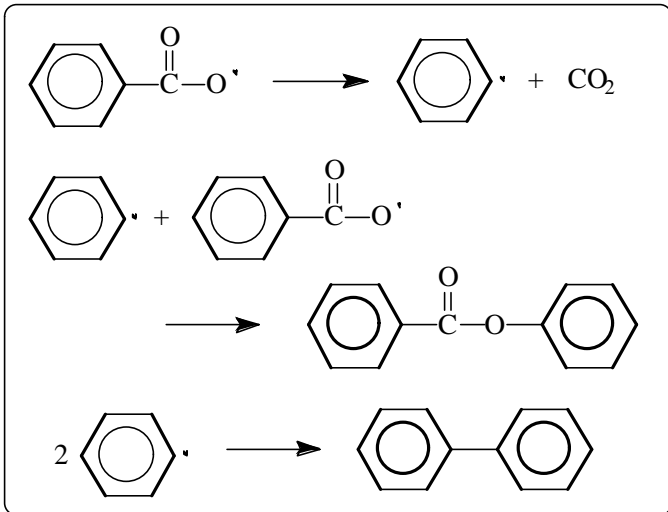$$R \cdot + M \xrightarrow{\text{k}_i} M_1 \cdot$$

ASSUME DECOMPOSITION IS THE RATE LIMITING STEP

i.e. $k_i \gg k_d$

THEN WE SHOULD ONLY HAVE TO CONSIDER k_d

i.e. $-\dfrac{d[\,I\,]}{dt} = \dfrac{1}{2}\dfrac{d[M_1 \cdot]}{dt} = k_d\,[\,I\,]$

BUT; ONLY A FRACTION f OF RADICALS INITIATE CHAIN GROWTH

$$r_i = \dfrac{d[M_i]}{dt} = 2\,f\,k_d[\,I\,]$$

PROPAGATION

$$M_1\cdot + M \xrightarrow{\;k_p\;} M_2\cdot$$

$$M_2\cdot + M \xrightarrow{\;k_p\;} M_3\cdot$$

In general;

$$M_x\cdot + M \xrightarrow{\;k_p\;} M_{x+1}\cdot$$

Assumption; reactivity is
independent of chain length

$$r_p \;=\; -\frac{d[M]}{dt} \;=\; k_p[\,M\,][\,M\cdot\,]$$

TERMINATION

COMBINATION

$$M_x^{\cdot} + M_y^{\cdot} \xrightarrow{\;\;k_{tc}\;\;} M_{x+y}$$

DISPROPORTIONATION

$$M_x^{\cdot} + M_y^{\cdot} \xrightarrow{\;\;k_{td}\;\;} M_x + M_y$$
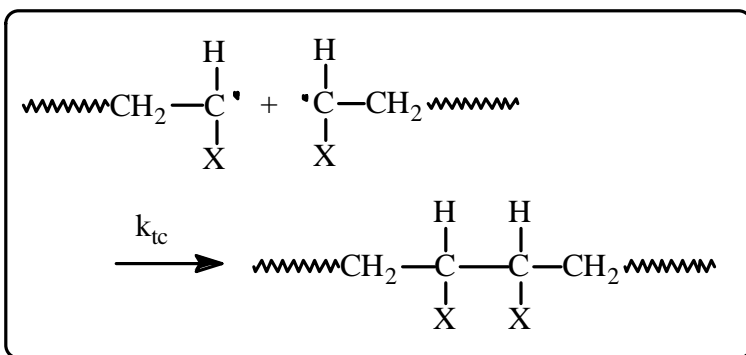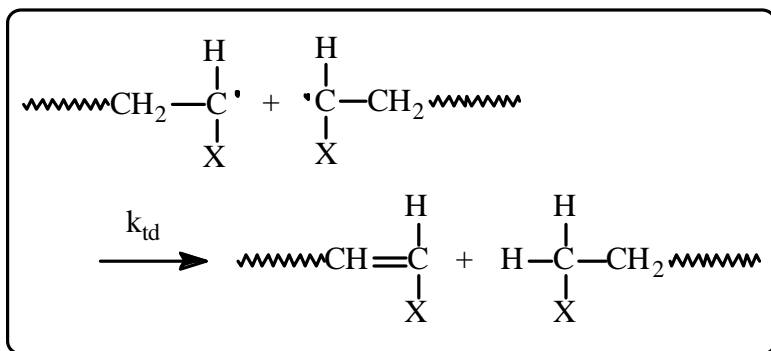
RATE OF TERMINATION

$$r_t = -\frac{d[M\cdot]}{dt} = 2 k_t [M\cdot][M\cdot]$$

Where $k_t = k_{tc} + k_{td}$

OBTAINED FROM :

- *Both reactions are second order*

- *Rate of removal of chain radicals = sum of the rates of the two termination reactions*

SUMMARY

$$r_i = \frac{d[M_1]}{dt} = 2\,f\,k_d\,[I]$$

$$r_p = -\frac{d[M]}{dt} = k_p\,[M][M\cdot]$$

$$r_t = -\frac{d[M\cdot]}{dt} = 2\,k_t\,[M\cdot][M\cdot]$$

PROBLEM :

We don't know $[M\cdot]$

SOLUTION :

Assume a steady state concentration of transient species

STEADY STATE ASSUMPTION

$[M\cdot] = CONSTANT$

*This means that radicals
are consumed at the same
rate as they are generated*

$$r_i = r_t$$

$$2f\, k_d\, [\, I\,] = 2\, k_t\, [\, M\cdot\,]^2$$

$$[\, M\cdot\,] = \left[\, \frac{f k_d\, [\, I\,]}{k_t}\, \right]^{1/2}$$

RATE OF PROPAGATION

RATE OF PROPAGATION = RATE OF POLYMERIZATION

$$r_p = R_p$$

substituting; $\quad r_p = k_p \left[\dfrac{f k_d [\,I\,]}{k_t} \right]^{1/2} [\,M\,]$

BUT [I] IS NOT CONSTANT.

from $\quad -\dfrac{d[\,I\,]}{dt} = k_d\,[\,I\,]\;$ *obtain* $\quad [\,I\,] = [\,I_0]\,e^{-k_d t}$

HENCE

$$R_p = \left[\, k_p \left[\dfrac{f\,k_d}{k_t} \right]^{1/2} [\,M\,][\,I_0\,]^{1/2} \right] \left[\, e^{-k_d t/2} \,\right]$$

WHAT DOES THIS TELL US ?

1. IF WE WANT TO INCREASE R_p
   INCREASE [M] OR [I]

2. $R_p \sim k_p / k_t^{1/2}$

3. TROMSDORFF EFFECT

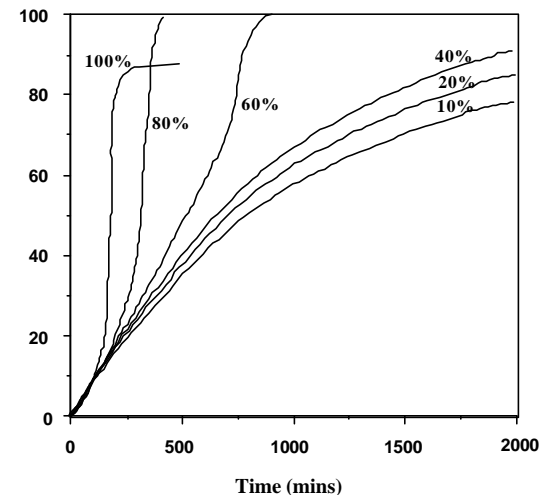*But; changing [I] also changes mol. wt. – more on this later !*

For ethylene at 130 ^{0}C and 1 bar pressure

$k_p / k_t^{1/2} \sim 0.05$

For ethylene at 200^0 C and 2500 bar pressure
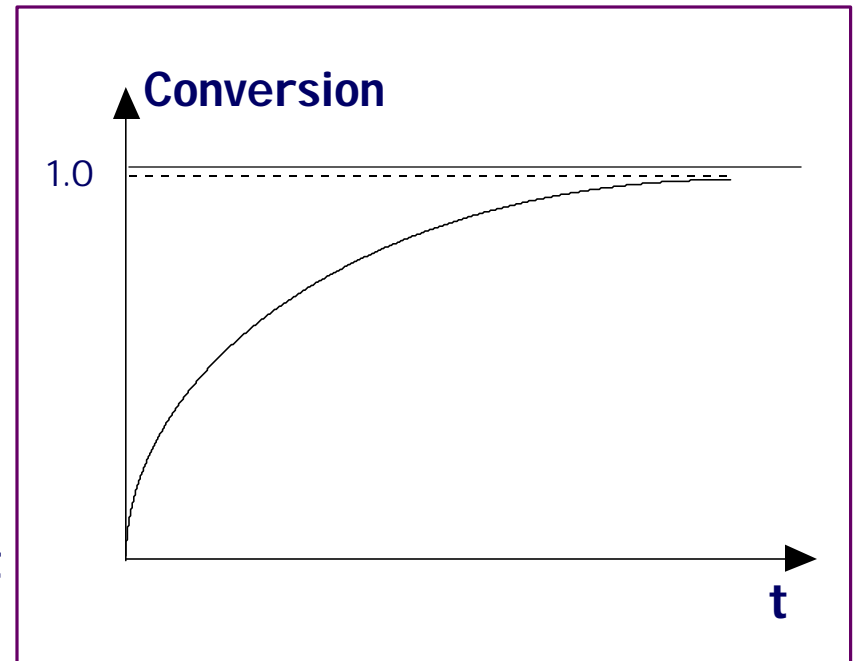
$k_p / k_t^{1/2} \sim 3.0$

CONVERSION

DEFINITION ; $\dfrac{[M_0] - [M]}{[M_0]}$ = $\dfrac{\text{Amount of monomer used up}}{\text{Amount of monomer at start}}$

in initial stages of reaction we can assume $[I] = [I_0]$ = *constant*

$$\frac{d[M]}{dt} = -k_p \left[\frac{fk_d[I]}{k_t} \right]^{1/2} [M]$$

Integrating

$$Ln \frac{[M]}{[M_0]} = -k_p \left[\frac{fk_d[I_0]}{k_t} \right]^{1/2} t$$

MAXIMUM CONVERSION

USUALLY THERE IS A FIRST ORDER DECAY IN INITIATOR CONCENTRATION

i.e. $\dfrac{d[I]}{dt} = -k_d[I]$ $\qquad\qquad$ $[I] = [I_0] e^{-k_d t}$

and

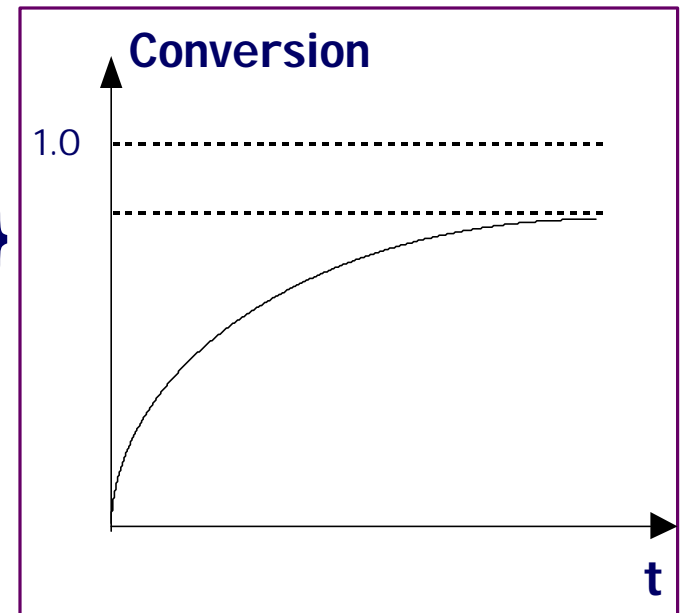$$Ln\ \dfrac{[M]}{[M_0]} = -\ \dfrac{2\,k_p}{k_d}\left[\dfrac{f k_d\,[I_0]}{k_t}\right]^{1/2}\left[1 - e^{-k_d t}\right]$$

hence

CONVERSION =

$$1 - \exp-\left\{2\,k_p\left[\dfrac{f\,[I_0]}{k_t\,k_d}\right]^{1/2}\right]\left[1 - e^{-k_d t/2}\right]\right\}$$

MAX CONVERSION (t $\longrightarrow$ ¥) =

$$1 - \exp-\left\{2\,k_p\left[\dfrac{f\,[I_0]}{k_t\,k_d}\right]^{1/2}\right\}$$

AVERAGE CHAIN LENGTH

DEFINE *KINETIC CHAIN LENGTH*

$$n \; = \; \frac{\text{RATE OF MONOMER ADDITION TO GROWING CHAINS}}{\text{RATE AT WHICH CHAINS ARE STARTED}}$$

This is the average number of monomers polymerized per chain radical at a particular instant of time during the polymerization

KINETIC CHAIN LENGTH

CONSIDER A TIME PERIOD   t

let us say that

1. 100 chains are started
2. 1,000,000 monomers are reacted
   in this time period

Then the average degree of
polymerization of these chains
is

$$\longrightarrow \quad \frac{1,000,000}{100} = 10,000$$

KINETIC CHAIN LENGTH

THERE WILL BE SOME OBVIOUS ERRORS (e.g. What about chains that were initiated, but did not terminate just before the start of the chosen period ?), BUT THESE DECREASE AS
t $\longrightarrow$ SMALL

IN THE LIMIT OF A TIME PERIOD dt

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

i.e. $n \sim \dfrac{[M]}{[I]^{1/2}}$ c.f. $r_p \sim [M][I]^{1/2}$

THE DEGREE OF POLYMERIZATION THEN DEPENDS UPON THE MECHANISM OF TERMINATION

$$\bar{x}_n = n \qquad \text{– disproportionation}$$
$$\bar{x}_n = 2 \, n \qquad \text{– combination}$$

INSTANTANEOUS NUMBER AVERAGE CHAIN LENGTH

What if termination occurs by both mechanisms ? define an average number of dead chains per termination reaction

$$x = \frac{\text{rate of dead chain formation}}{\text{rate of termination}}$$

$$= \frac{[2 k_{td} + k_{tc}][M\cdot]^2}{[k_{td} + k_{tc}][M\cdot]^2} = \frac{[2 k_{td} + k_{tc}]}{k_t}$$

HENCE

$$\overline{x}_n = \frac{k_p [M\cdot][M]}{[2 k_{td} + k_{tc}][M\cdot]^2}$$

$$\overline{x}_n = \frac{k_p [M]}{x [f k_d k_t]^{1/2} [I]^{1/2}}$$

CHAIN TRANSFER
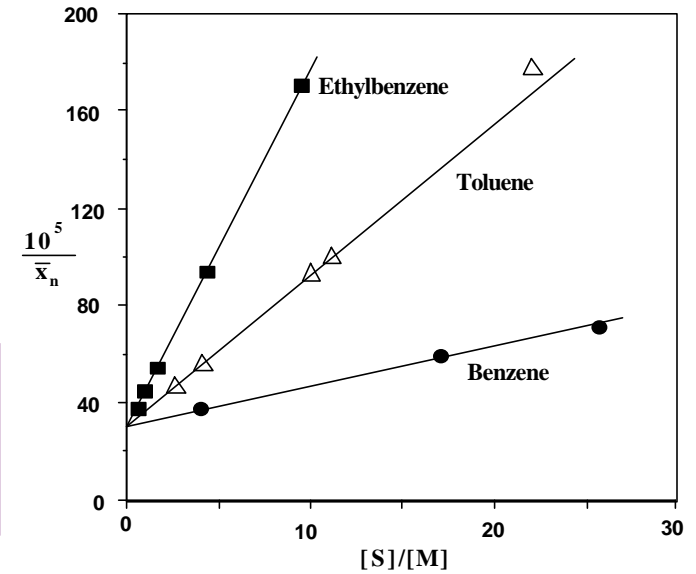
Chain transfer can occur to solvent, added agents, etc.

$$R' : H + M_x \cdot \longrightarrow M H_x + R' \cdot \qquad r_{tr} = \frac{d[M \cdot]}{dt} = - k_{tr} [R':H][M \cdot]$$

$$-\frac{d[M \cdot]}{dt} = 2k_{td}[M^2 \cdot] + k_{tc}[M^2 \cdot] + k_{tr}[T][\cdot M]$$

CAN THEN OBTAIN

$$\overline{x}_n = \frac{k_p [M]}{\mathbf{x} [f k_d k_t]^{1/2} [I]^{1/2} + k_{tr}[T]}$$

OR

$$\frac{1}{\overline{x}_n} = \frac{1}{(\overline{x}_n)_0} + \frac{C[T]}{[M]} \qquad \text{where } C = k_{tr} / k_p$$

Redrawn from the data of R.A.Gregg + F.R.Mayo, Faraday Soc. Discussions,2,328(1947)