

4. Addition Polymerisation

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4.1 Introduction

Addition, (free radical) polymerisation.

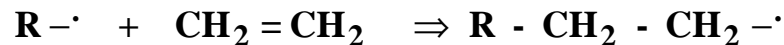
(has certain similarities to life. "Birth" → propagation → death)

Start with initiator, a molecule with a free radical. Unpaired electron.

R·

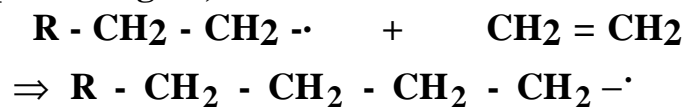
Introduce monomer containing C = C bond.

Reaction opens double bond, monomer inserts onto initiator.



Free radical propagates to end of chain

Repeat process again,



repeat process again and again and.....

Chain growth terminates by another reaction to form "dead" chain

Reaction involves three steps

Initiation

Propagation

Termination

The plan,

Construct reaction scheme that can predict

a) Yield

b) MM distribution (\overline{DP}_n or $\equiv \overline{M}_n$ only)

c) Give insight into reactor options

4.2 Addition, (free radical) polymerisation reaction scheme

Most industrial addition polymerisations involve a catalytic reaction which is not fully understood and is difficult to model.

We developed a "simple" scheme from which we can easily get \overline{DP}_n or \overline{M}_n but unable analytically to obtain whole distribution.

Scheme

homopolymer - single monomer species

no catalyst

Symbols

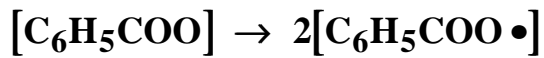
M = monomer molecule

**M_r = fully grown dead polymer of r repeat units and
mm $M = M_{0r}$ ($M_r = M_m$)**

P_r = A living polymer of r repeat units (i.e., a polymer with a reactive chain end).

**Let R_i = rate of generation of free radical initiator
monomer fragment i.e., a P_1**

4.3 Initiation



$$R_i = k_i [m] [I]$$

[I] = initiator conc

c) **Other mechanisms**

$$R_i = k_i [m]^n$$

Where $n = 2$ or 3 .

d) **Also**

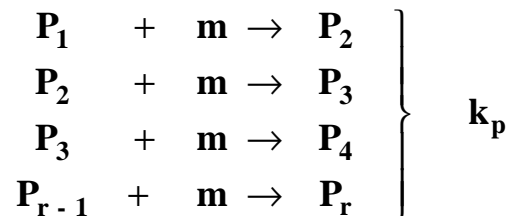
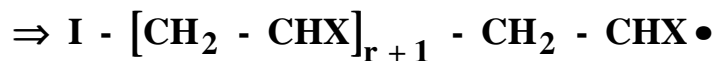
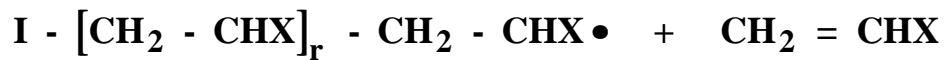
$$R_i = k_i [m] [uv]$$

[uv] = light intensity

Remember,

There are a number of different ways initiation can occur.

4.4 Propagation



k_p is assumed to be independent of r (i.e., mm)

Ex. rate of loss of P_2

$$-\frac{dP_2}{dt} = k_p[M][P_2] - k_p[M][P_1]$$

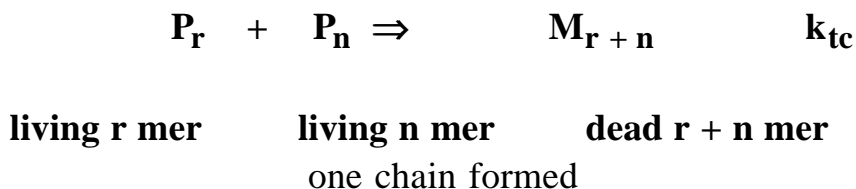
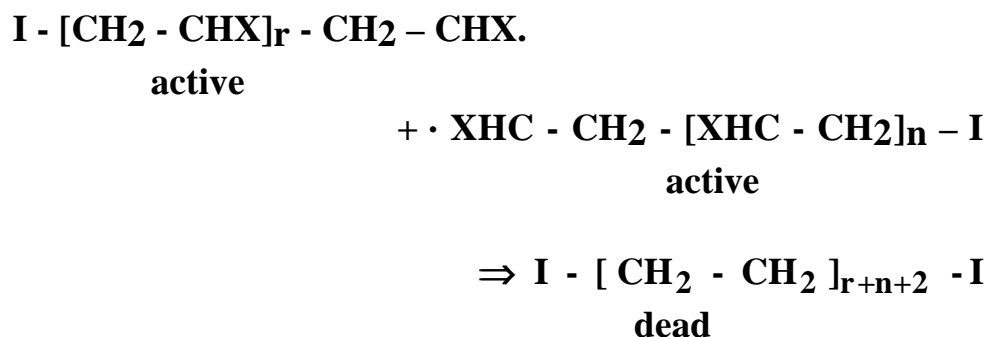
Remember

4.5 Termination,

There are a number of possibilities.

a) Termination by combination.

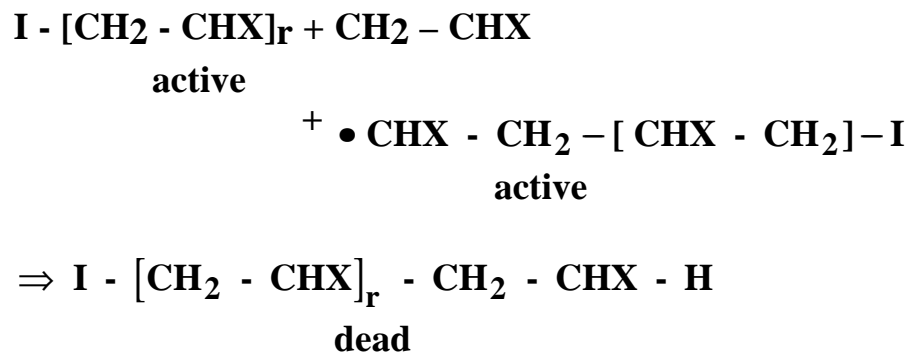
Coupling of two active radicals to form one dead chain.



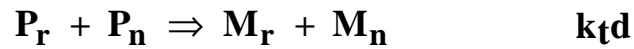
$$- \frac{dP}{dt} = k_{tc} [P] [P]$$

b) Termination by disproportionation,

Two growing chains form two dead chains



dead



Two chains formed

$$-\frac{dP}{dt} = k_{td} [P] [P]$$

c) Chain transfer (see later).

Note

k_i initiation

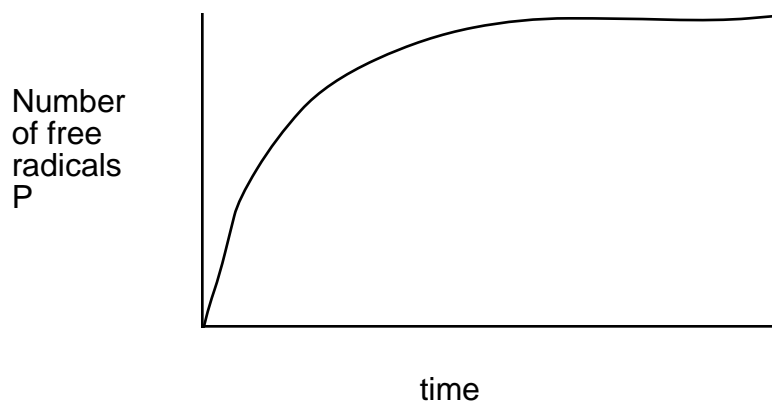
k_p propagation

k_t , either k_{tc} and or k_{td} termination

are all "normal" chemical rate constants and have "normal" temperature dependences.

4.6 The "Steady state" assumption.

Analysis of above scheme: Use the "steady state assumption".
"During polymerisation, numbers of active species (free radicals) does not change".



Free radicals “move” along chain.

Free radicals are “lost” with the termination process.

Proof of steady state assumption.

At any stage in the polymerisation we have a range of species.

$[P_1]_s, [P_2], [P_3]_s, \dots, [P_n]_s, \dots$

Let, $P = \sum [P_n]$ total number of active species

$$\frac{dP}{dt} = + \left[\text{term due to initiation} \right] \pm \left[\text{term due to propagation ?} \right] - \left[\text{term due to termination} \right]$$

Initiation, $+ R_i$

Propagation zero transfer of P_n to P_{n+1}
will not change total number of P_s .

Termination

Rate of loss of P_r type active chain to other P_s .

$$= - \{ k_t P_1 P_r + k_t P_2 P_r + k_t P_3 P_r + \dots k_t P_n P_r + \dots \}$$

$$= - \{ P_r \sum P_n = - \{ k_t P_r P \}$$

$$\text{where } P = \sum P_n$$

Rate of loss of all active chains

$$= - \{ k_t P_1 P + k_t P_2 P + k_t P_3 P + \dots k_t P_n P + \dots \}$$

$$= - k_t P \sum P_n = - k_t P^2$$

So

$$\frac{dP}{dt} = R_i + 0 - k_t P^2$$

change in P initiation Prop. Termination

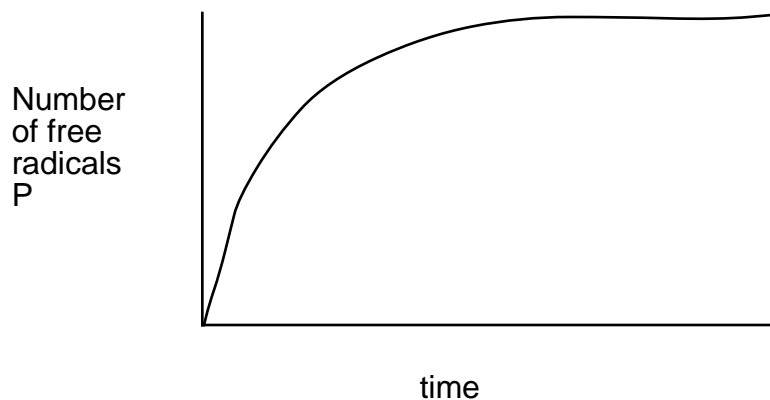
$$\frac{dP}{R_i - k_t P^2} = dt$$

Standard $\int \frac{dx}{1 - cx^2} = \frac{1}{c^{0.5}} \tanh^{-1} c^{0.5} x$

$$P = \left[\frac{R_i}{k_t} \right]^{0.5} \tanh \left(\left[R_i k_t \right]^{0.5} t \right)$$

A) Growth Let $P = 0$ at $t = 0$
 $P = P_\infty$ at $t = \infty$

$$P = P_\infty \tanh \left(\frac{t}{\tau_1} \right)$$



Time const. $\tau_1 = \frac{1}{\left[R_i k_t \right]^{1/2}}$ $P_\infty = \left[\frac{R_i}{k_t} \right]^{1/2}$

B) Decay

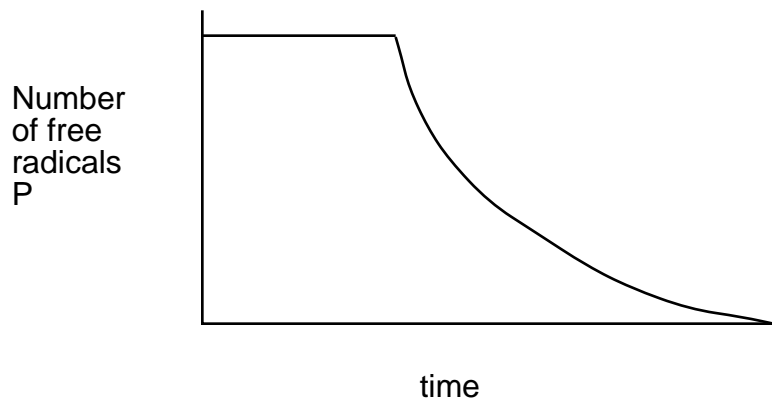
After a long time, let R_i abruptly drop to zero (ex. UV switch off radiation).

Governing ODE
$$\frac{dP}{dt} = -k_t P^2$$

$$k_t t = \frac{1}{P} - \frac{1}{P_\infty}$$

or
$$P = P_\infty \left[\frac{1}{1 + (R_i k_t)^{1/2} t} \right]$$

$$\tau_2 = \frac{1}{(R_i k_t)^{1/2}}$$



Measure τ_2 experimentally easier? Then τ_1 usually

$$\tau_2 = \tau_1 \sim 10^{-2} - 10^{-3} \text{ s.}$$

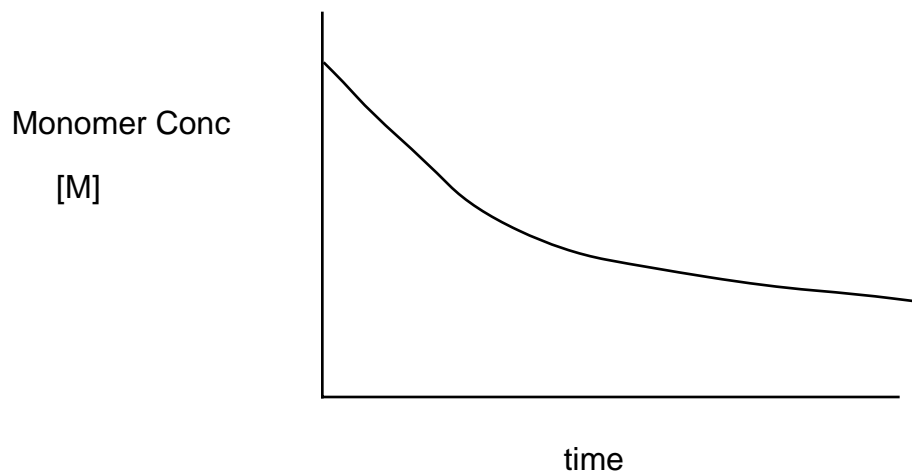
\therefore time to reach steady state (10^{-2} s) is very much less than reaction times $\sim 10^2 - 10^3$ secs.

If in steady state, then
$$\frac{dP}{dt} = 0$$

and
$$R_i = k_t P^2$$

$$P = \left[\frac{R_i}{k_t} \right]^{1/2}$$

However, P may change with time



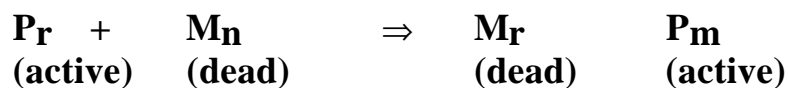
A useful equation that can usually be applied to additional polymerisation problems.

Note batch reaction R_i may change with time but quasi ss still equation applies.

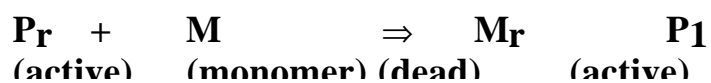
4.7 Complications,

Chain Transfer

Transfer process in which reactivity of a growing entity is transferred to some other species.

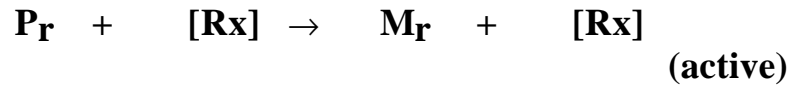


activity changed from one chain to another.



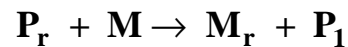
activity changed for one chain to monomer.

In general

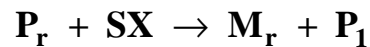


RX can be a molecule of

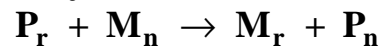
a) **Monomer k_m**



b) **Solvent k_s**

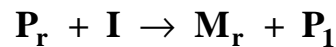


c) **Polymer**

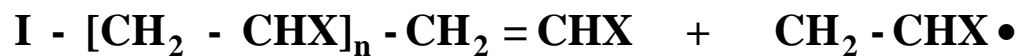
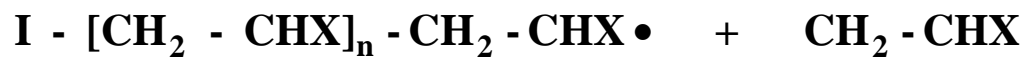


in "theory" but not in practice

d) **Initiator**

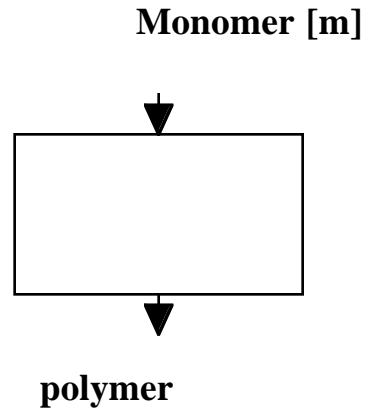


Example Chain transfer to monomer



Handout 2. Addition

The reaction pot.



Monomer consumed

$$\frac{d[M]}{dt} = -k_p[M][P]$$

Rate of termination

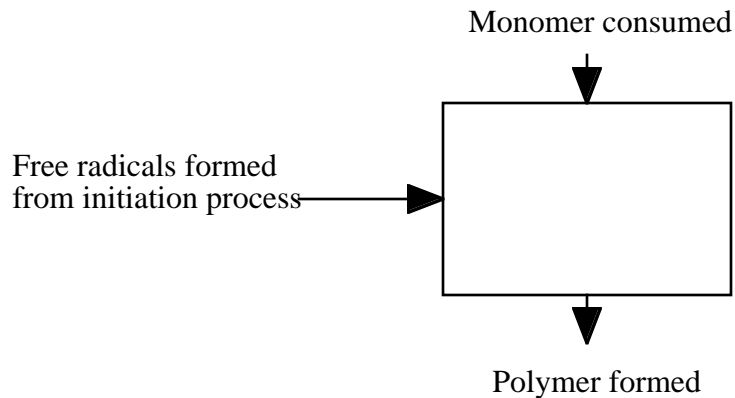
$$k_t[P]^2$$

$$P = \sum P_i$$

After $\sim 10^{-2}s$ of reaction we are in steady state

$$\frac{dP}{dt} = 0$$

So we can perform a dynamic "mass balance".



Define kinetic chain length

$$\gamma = \text{number of propagation steps that}$$

of one free radical.

In steady state

$$\gamma = \frac{\text{Rate of consumption of monomer}}{\text{Rate of initiation of free radicals}}$$

$$= \frac{k_p [M] [P]}{R_i}$$

$$\text{where } P = \sum P_r$$

γ is related to $\overline{DP}_n \rightarrow$ see later!

4.8 Determination of \overline{DP}_n for addition polymerisation

[\overline{DP}_n in this case relates to the \overline{DP}_n of polymer being formed, excludes the monomer].

$$\overline{DP}_n = \frac{\sum N_r r}{\sum N_r}$$

$$= \frac{\text{total number of repeat units in population}}{\text{total number of molecules in population}}$$

We are in "steady state"

$$\overline{DP}_n = \frac{\text{rate of consumption of repeat units}}{\text{rate of formation of molecules}}$$

$$\overline{DP}_n = \frac{k_p [P] [M]}{k_m [P] [M] + k_s [P] [SX] + \frac{1}{2} k_{tc} [P]^2 + k_{td} [P]^2} \quad (1)$$

chain transfer to monomer

termination by combination

termination by disproportionation

a) Ignore chain transfer to initiator

Introduce steady state assumption eqn.

$$R_i = k_t [P]^2 = k_{tc} [P]^2 + k_{td} [P]^2$$

$$\begin{aligned} \text{So } \frac{1}{2} k_{tc} [P]^2 + k_{td} [P]^2 &= \frac{1}{2} R_i + \frac{1}{2} k_{td} [P]^2 \\ &= \frac{R_i}{2} \left[1 + \frac{k_{td}}{R_i} [P]^2 \right] \\ &= \frac{R_i}{2} \left[1 + \frac{k_{td}}{k_{tc} + k_{td}} \right] \end{aligned}$$

Sub. ss eqn. into master eqn.

$$\frac{1}{\overline{DP}_n} = \frac{k_M}{k_p} + \frac{k_s[SX]}{k_p[M]} + \frac{1}{2\gamma} \left[1 + \frac{k_{td}}{k_{tc} + k_{td}} \right]$$

$$\text{where } \gamma = \frac{k_p [M] [P]}{R_i}$$

Notes



Chain transfer to monomer (strongly active mechanism for PVC)



Chain transfer to solvent (Independent way of controlling MW in solution polymerisation was used PE soln process).



1/2 avoids double counting $P = \sum P_i$
 termination by combination

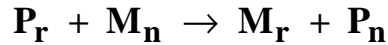
rate of polymer formation = 1/2 rate of termination

$$d) \quad \frac{1}{2} 2 k_{td} [P]^2 \qquad P_r + P_m = M_r + M_n$$

1/2 avoids double counting 2, takes into account 2 chains formed.
 Termination by disproportionation.

Rate of polymer formation = rate of termination

e) Chain transfer to polymer



Possible but does not generate net inc. in chains. DP_n not effected
 but term will influence whole N_r distribution.

Ignore chain transfer

$$\text{Then} \quad \frac{1}{\overline{DP}_n} = \frac{1}{2\gamma} \left[1 + \frac{k_{td}}{k_{tc} + k_{td}} \right]$$

Termination by combination only $k_{td} = 0$

$$\frac{1}{\overline{DP}_n} = \frac{1}{2\gamma} \qquad \overline{DP}_n = 2\gamma$$

Termination by disproportionation only $k_{td} = k_t$

$$\frac{1}{\overline{DP}_n} = \frac{1}{\gamma} \qquad \overline{DP}_n = \gamma$$

half the above value

$$\overline{DP}_n = k_p \frac{[M][P]}{R_i}$$

$$\text{Steady state} \quad [P] = \left[\frac{R_i}{k_t} \right]^{1/2}$$

Let (for example) $R_i = k_i [M] [I]$

Then

$$\overline{DP}_n = \frac{k_p}{k_t^{1/2} k_i^{1/2}} [M]^{1/2} [I]^{-1/2} \quad *$$

\overline{DP}_n depends on ratio $\frac{k_p}{k_t k_i}$

" weakly depends on monomer and initiation conc.

For high MM k_p large, k_i small.

Often with additional polymerisation the problem is to keep MW down.

When chain transfer is present.

DP_n is decreased

$$\frac{1}{\overline{DP}_n} = \frac{k_M}{k_p} + \frac{k_s [SX]}{k_p [M]} + \frac{1}{2\gamma} \left[1 + \frac{k_{td}}{k_{tc} + k_{td}} \right]$$

Monomer Solvent

chain transfer transfer. Can be used as independent control of MW.

PVC.

Styrene

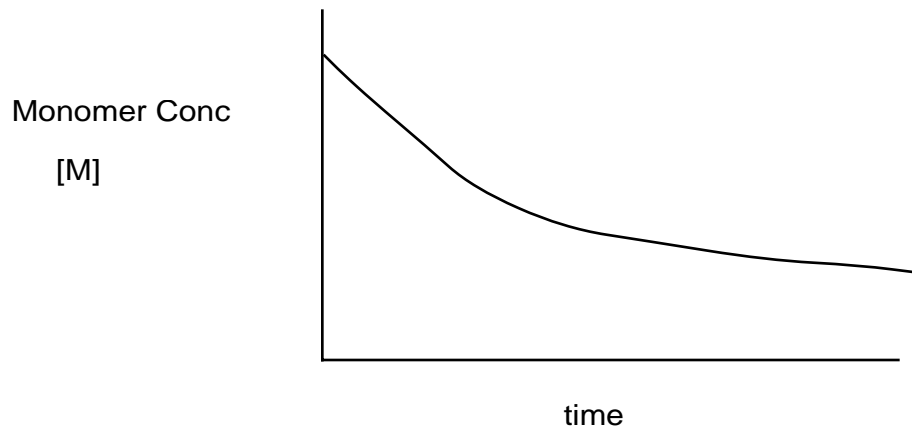
Solvent	[X]	k_s/k_p
benzene	C_6H_6	0.018
toluene	$C_6H_6CH_3$	0.125
CTC	CCl_4	90 big

Viable way for MM control in solution polymerisation.

Gas phase polymerisation HDPE.

4.9 Batch conversion kinetics for addition polymerisation

Best followed by looking at rate of monomer consumption [m].



$$-\frac{d[M]}{dt} = k_p [M] [P]$$

Assume steady state at any time t.

$$R_i = k_t [P]^2$$

(Note both R_i and P may be changing during polymerisation but ss eqn. is assumed to hold.)

Assume (say) $R_i = k_i [M] [I]$

$$\text{Then } -\frac{d[M]}{dt} = k_p \left[\frac{k_i}{k_t} \right]^{1/2} [M]^{3/2} [I]^{1/2}$$

$$-\frac{d[M]}{dt} = k_o [M]^{3/2} [I]^{1/2}$$

k_o = overall constant

Assume (say I is a const. during polymerisation)

Then

$$M_0 \left[\frac{1}{M^{1/2}} \right] = \frac{k_0 [I]^{1/2}}{2} t$$

$$\frac{1}{M^{1/2}} - \frac{1}{M_0^{1/2}} = \frac{k_0 [I]^{1/2}}{2} t$$

Batch addition

Let conversion $P_c = P_c = \left[1 - \frac{M}{M_0} \right]$

$$\left. \begin{array}{l} M = M_0 \quad P_c = 0 \\ M = 0 \quad P_c = 1 \end{array} \right\}$$

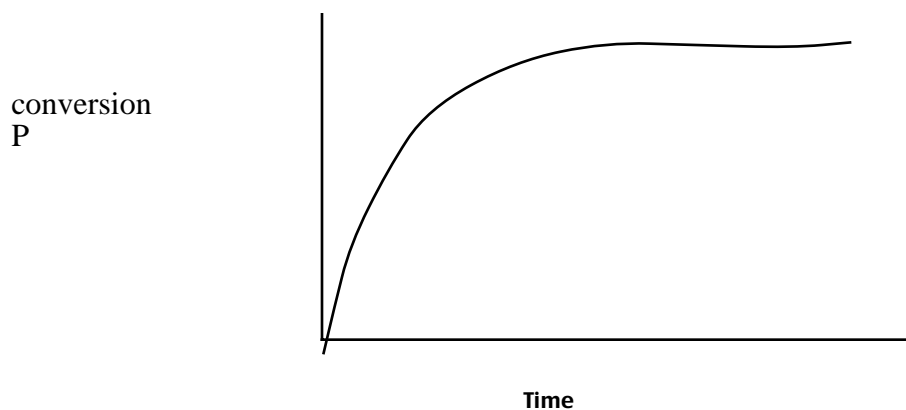
Then

$$P_c = \frac{[1 + \beta t]^2 - 1}{[1 + \beta t]^2}$$

where $\beta = \frac{M_0^{1/2} k_0 [I]^{1/2}}{2}$

Overall conversion kinetics

Similar to stepwise.



Progressive conversion with time. No surprises here.

Change in MM during polymerisation

Assume (say) no chain transfer and k_{tc} only.

$$\overline{DP}_n = 2\gamma = \frac{2k_p}{R_i} [M] [P]$$

using (say) $R_i = k_i [M] [I]$
ss. $R_i = k_t [P]^2$

$$\overline{DP}_n = \frac{2k_p}{k_t^{1/2} k_i^{1/2}} [M]^{3/2} [I]^{1/2}$$

as monomer conc. decreases \overline{DP}_n will also decrease but, unlike
Stepwise polymerisation we are making high MM from beginning of
polymerisation:- for $\sim 10^{-2}$ s reaction

Batch addition

Time has big effect on conversion, but relatively small effect on MM.

MM controlled largely by $\frac{k_p}{R_i^{1/2} k_i^{1/2}}$

The Big Issue

Stepwise

Slow build up of \overline{M}_n

Slow build up of P

Addition

Slow build up of P.

Polymer, decent \bar{M}_n being formed right from the word go.

4.10 What temperature do you run reactors at?

Temperature effects

* rate of conversion

* MMD i.e., \bar{DP}_n

1) Yield

$$-\frac{d[M]}{dt} = k_p [M] [P]$$

ss. $R_i = k_t [P]^2$

assume (say) $R_i = k_i [M] [I]$

Then

$$-\frac{d[M]}{dt} = k_p \left(\frac{k_i}{k_t} \right)^{1/2} [M]^{3/2} [I]^{1/2}$$

$$k_{\text{overall}} = k_p \left(\frac{k_i}{k_t} \right)^{1/2} = k_{\text{overall}} [M]^{3/2} [D]^{1/2}$$

$$k_x = A_x e^{-E_x/RT}$$

$$E_{\text{overall}} = E_p - \frac{1}{2} E_t + \frac{1}{2} E_i$$

Typical values

E_p	~	30 kJ/mol
E_t	~	10 kJ/mol
E_i	~	110 kJ/mol

E_{overall} is positive.

$$k_0 = A e^{-E_0/RT}$$

Rate of polymerisation increases with increasing temperature.

Beware:- Reaction may be exothermic - heat removal
High temperature - side reactions

Often $T_R \sim 80 - 200^\circ\text{C}$ Typically 100°C

Effect of T on \overline{DP}_n

Consider no chain transfer and k_{tc} only.

$$\overline{DP}_n = 2\gamma = 2k_p \frac{[M] [P]}{R_i}$$

$$SS + R_i = k_i [m] [I]$$

$$\overline{DP}_n = 2 \frac{k_p}{k_t^{1/2} k_i^{1/2}} [M]^{3/2} [I]^{1/2}$$

$$k_0 = A_0 e^{-E_0/RT}$$

$$E_0 = E_p - \frac{E_t}{2} - \frac{1}{2} E_i$$

~ 30 - 5 - 55

E_0 is negative

So, increase T means In \overline{DP}_n

Molecular Mass Distribution

We have evaluated $\overline{DP}_n \equiv \overline{M}_n$

Difficult to derive \overline{M}_w , we need numerical techniques.

For addition polymerisation

$$\frac{\overline{M}_w}{\overline{M}_n} > 2 \quad \text{and often in range } 3 - 10$$

Much more polydisperse than stepwise.

Data sometimes fits. Log normal distribution.

$$w(M) = \frac{1}{\beta\pi^{1/2}} \frac{1}{M} \exp\left\{-\frac{(\ln(M/M^1))^2}{\beta^2}\right\}$$

where M^1 is parameter.

Sometimes data presented as Cummulative weight fraction.

$$W_M = \sum_0^M w(M) = \int_0^M w(M) dM$$

Wt frac of pop with $MM > M$

Physical state of polymer dominates choice of downstream separation processing and reactor design strategy.

Effect of T on Physical form

Ex. PE

PE in solvent (say xylene)

T = 120°C PE dissolves in solvent

T = 110°C Soln process

T = 100°C PE precipitates out of soln. Slurry process

Slurry process easier downstream separation

Addition Temperature strategy

High Temp

Fast kinetics

lower MM

Soln

(separation difficult)

Low Temp

Slower kinetics

to process)

(lower heat loads)

(separation easier)

Higher MM

(difficult to polymer

Precipitate

Conversion

High P_c would be nice → but (unlike stepwise) is not essential as we are making high MMD material from start.

Level of P_c controlled by "viscosity"/handling of polymer. Often $P_c \sim 0.3$.

4.11 Polymer production.

Where the science came first.

Carruthers:-1920s esterification of difunctional molecules.

(Dupont) Thought about mechanism in terms of polymer production.

1930s. Discovered Nylon, PET, Late 30's. Suicide

Dupont went on to become world leaders in Nylon.

Stepwise is generally a batch process. Technology not changed too much over the last few decades.

Where the experiment came first.

Polyethylene two "chance" discoveries

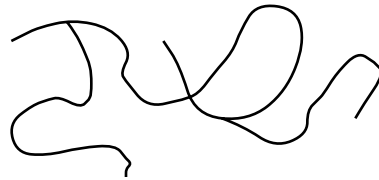
There are "three" types of PE.

a) Low density polyethylene. (LDPE)

1933. Fawcett & Gibson.

Manufacture at high pressure
branched.

Low crystallinity = low density



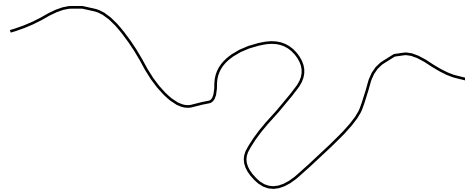
Long chain branching

b) High density polyethylene (HDPE)

1956. Zeigler Natta.

Manufactured at modest pressure

Linear, High crystallinity = high density

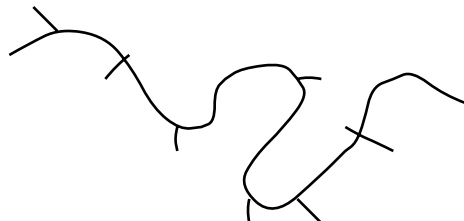


c) Linear low density polyethylene (LLDPE)

1970s Short chain branching

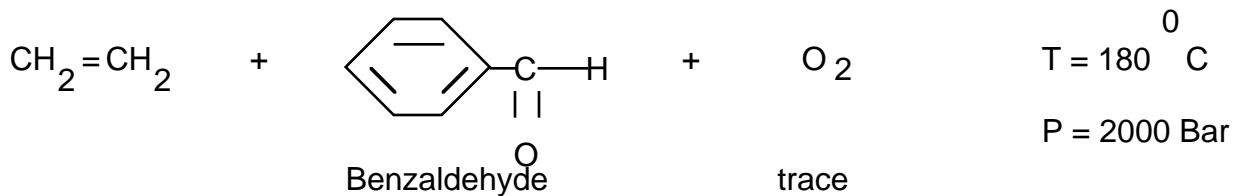
intermediate crystallinity = intermediate density

side branches PE or other molecule.



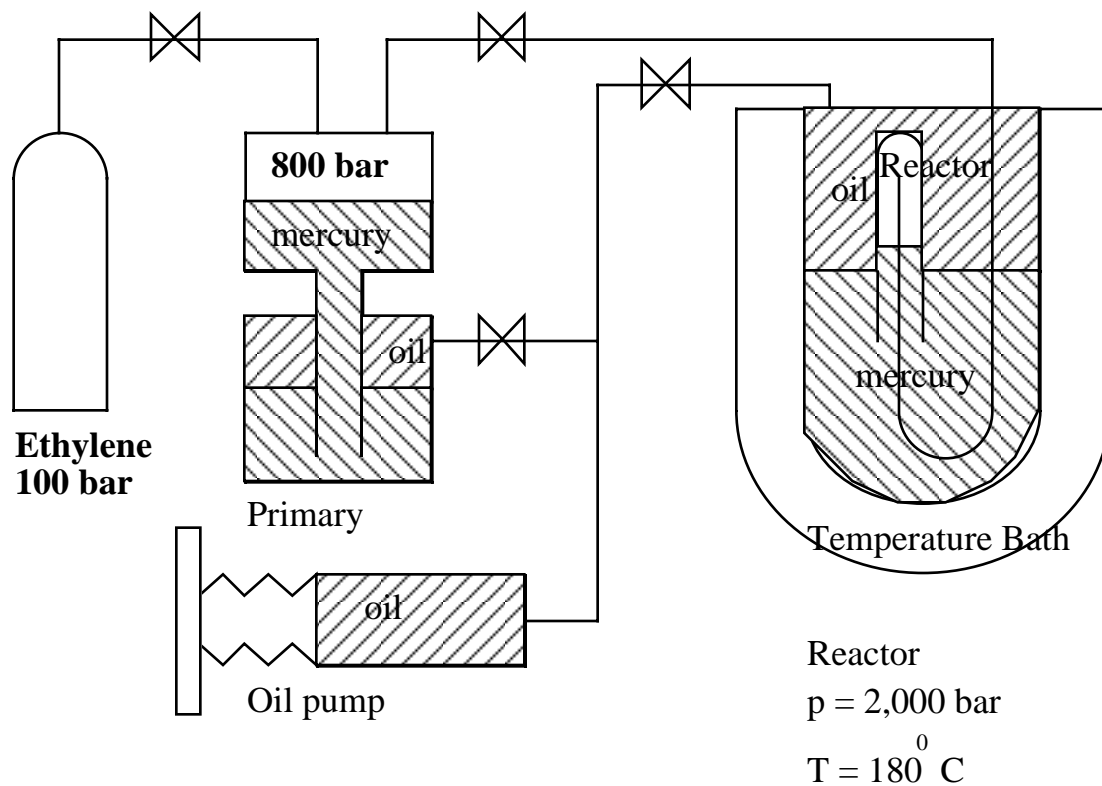
1933 ICI Winnington Hall. Fawcett and Gibson carried out systematic experiments on the effect of pressure on the kinetics of reactions.

Initially Liquid/ liquid reactions, no effect
 then, Liquid /gas reactions. they discovered a waxy material in the reactor which they later identified as a polymer polyethylene.



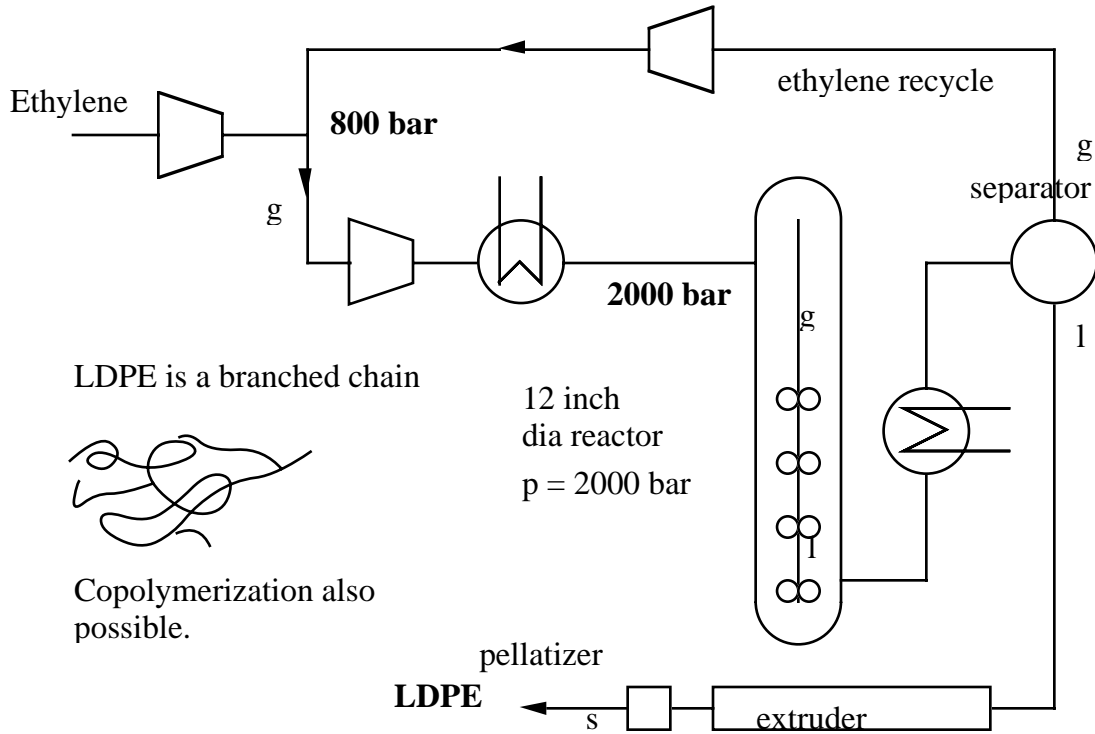
found 3g waxy solid in reaction vessel
 Two years later they had made 5g; it took them that long to realise the oxygen was required as an initiator.

Five years later; **30 tonnes /year!**
 1990s **10 000 000 tonnes /year**

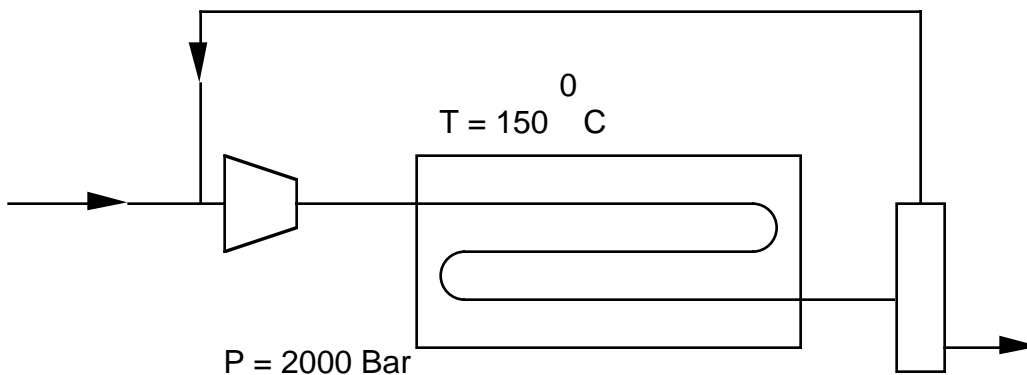


Current commercial manufacture of LDPE

LDPE ICI high pressure autoclave.

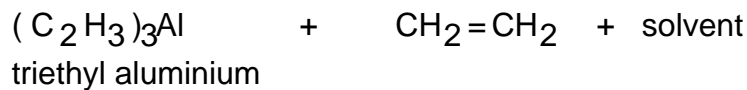


2. BASF. Plug flow reactor.



The high density polyethylene accident.

1953 Carl Zeigler. a Physical chemist, was carrying out experiments on the catalytic reaction of metal alkyls on organic molecules.



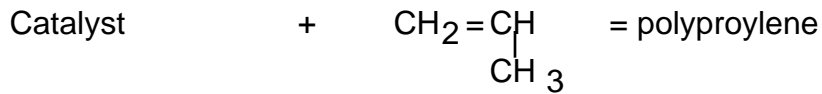
+ titanium chloride

(an accident , a residue from a previous experiment!)

P = 1 bar. T = 130 centigrade

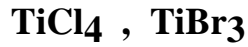
reaction yielded linear polyethylene

Later with Natta, (an Italian!).

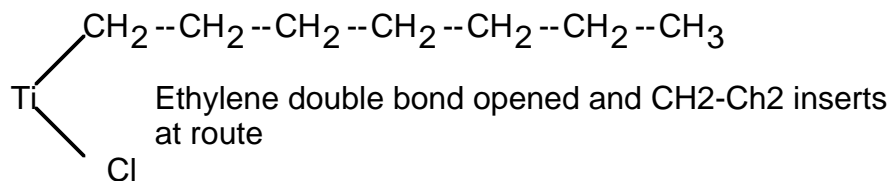
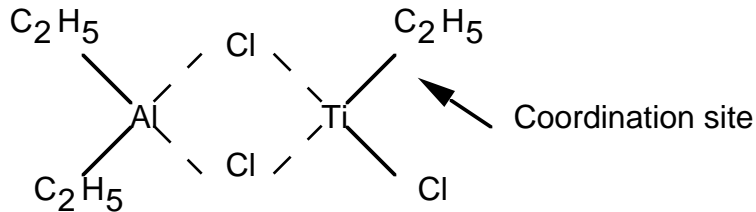


later, Zeigler Natta Catalysts

Metal Alkyls (1, 1,1,1) + transition metal compounds (1V, V11)

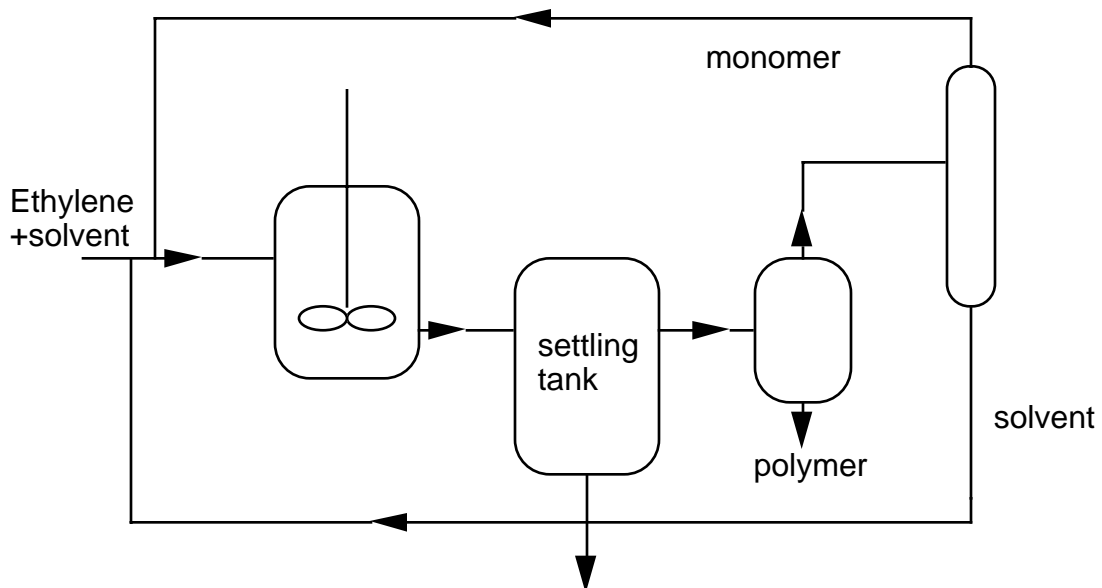


Form metal complexes such as
Tiethyl aluminium and Titanium trichloride.

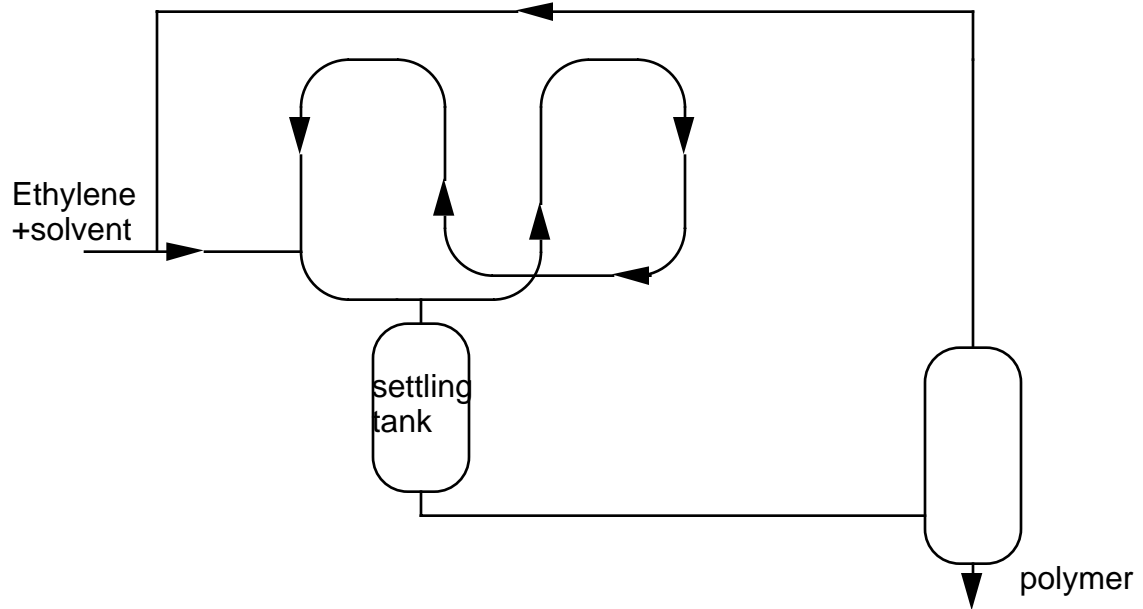


HDPE reactor evolution.

1960s. Solution process, with catalyst recovery.



Later, in the 70s. The Phillips "slurry" reactor.



In the 1990s. Fluid bed reactors. Union Carbide (Now Dow) and Bp.