

3. Stepwise Polymerisation

- 3.1 Functionality and polymerisation
- 3.2 Laboratory experiments kinetics
- 3.3 "Simple" derivation of \overline{DP}_n
- 3.4 Derivation of full MMD
- 3.5 Derivation of \overline{DP}_n from MMD
- 3.6 Derivation of \overline{DP}_w from MMD
- 3.7 Molecular mass control in stepwise polymerisation
- 3.8 Stabiliser addition
- 3.9 Time evolution of MMD
- 3.10 Summary

This is an important bulk commodity polymerisation route and it is also interesting in that relatively simple mathematical descriptions of molecular mass distributions can be derived.

Stepwise polymerisation is sometimes known as "condensation polymerisation". It is a polymerisation mechanism thought up by **Caruthers in the 1930's** who worked for Dupont. His discoveries marked the birth of polymer science and Dupont built up a world dominance in Nylon and PET based on his discovery.

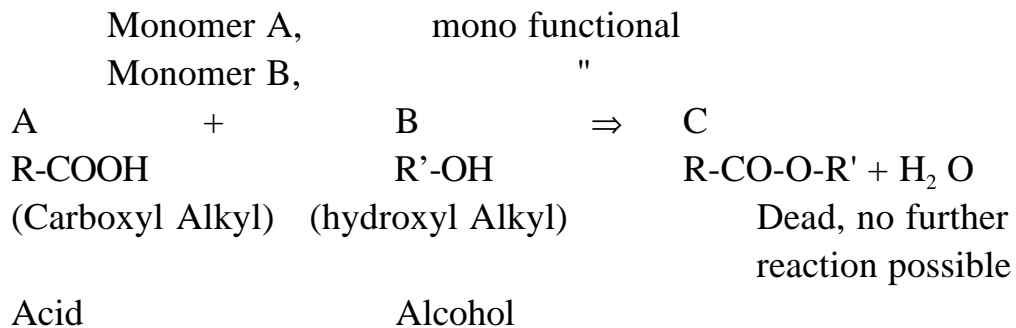
Some of the "big" stepwise polymers are,

Polyesters	-CO-O -	group in main chain
Polyamides	-CO-NH - R	" " "
Silicones	-SI-O - R	" " "

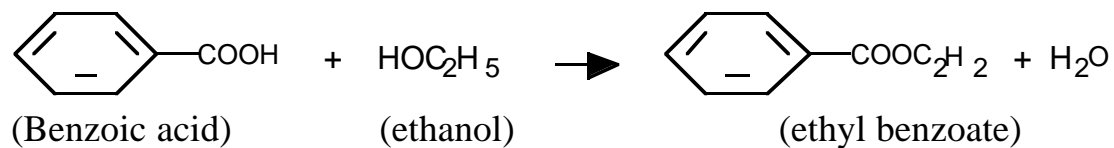
A stepwise polymer is where a poly functional molecule combines with its own species or another poly functional molecule to form a polymer and usually a small molecule (which is often water).

3.1 Monomer functionality and polymerisation

a) Esterification. No polymerisation.

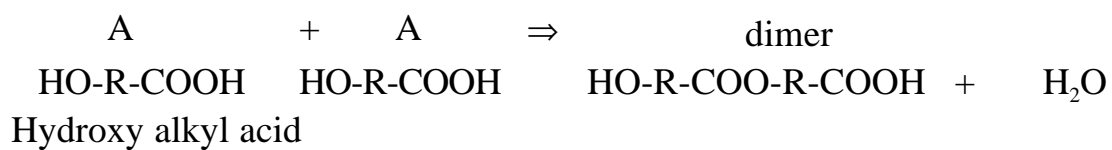


Example



b) Linear polymer chain

Single Monomer species A, functionality of 2, but requires different functional group at each of monomer



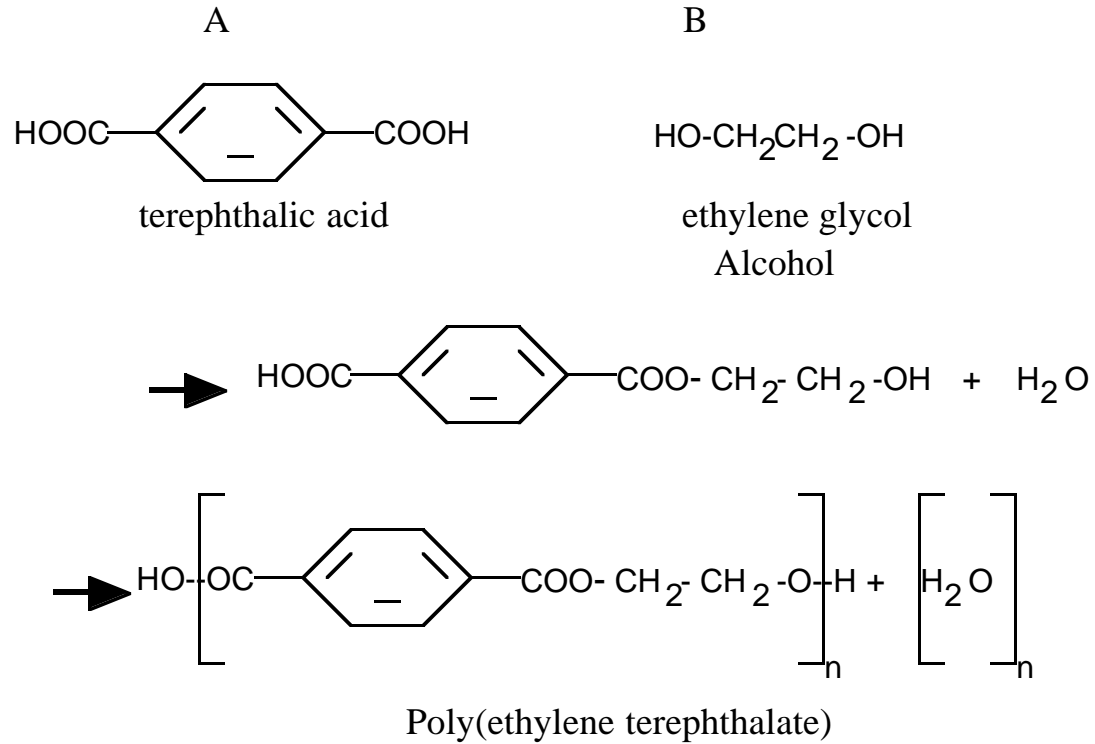
New molecule can react with monomer or other "chains"



c) Linear polymer chain by two di function monomers.

(usually cheaper than b)

Monomer A, functionality of two same end groups
Monomer B, functionality of two, same end groups

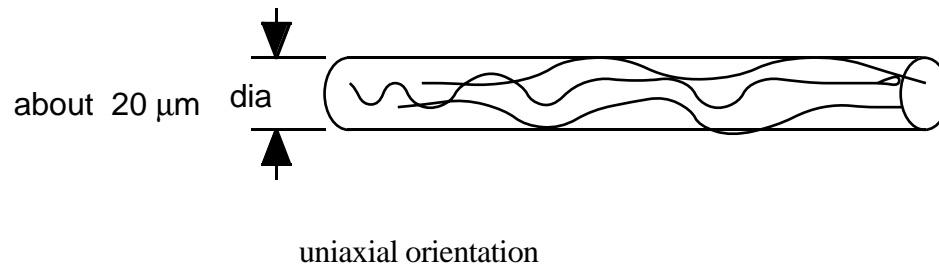


Thermoplastic
crystalline

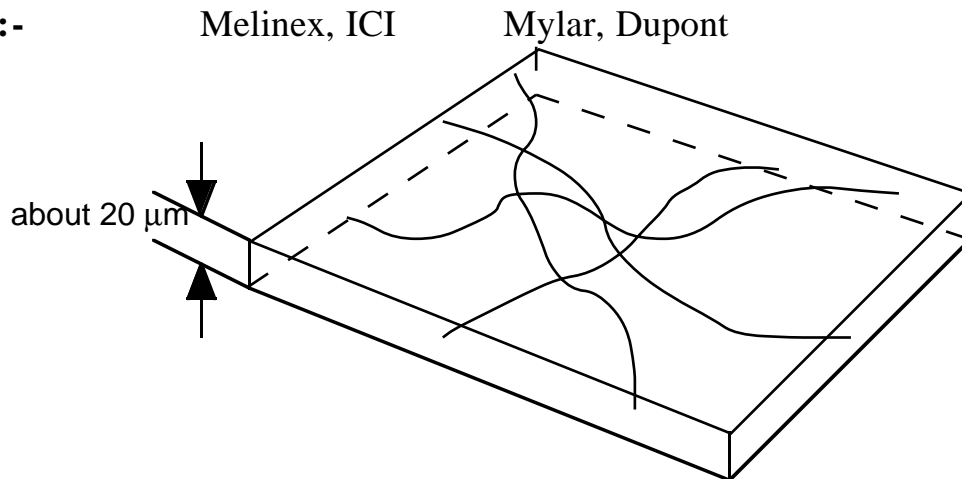
$T_m = 250^\circ\text{C}$

Semi

Fibre:- lowish viscosity → high spin speeds 10 - 100 m/s
Terylene ex ICI, Dacron, Dupont

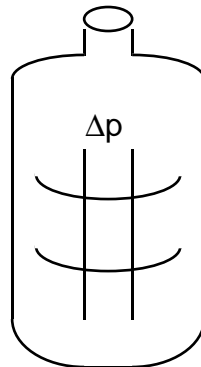
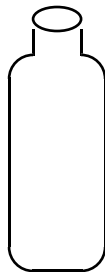


Film:-



Biaxial orientation

PET Bottle



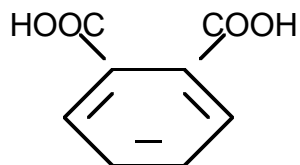
about 20 μm thickness

Injection moulded Preform.

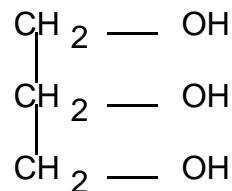
Biaxially oriented blown bottle

d) Network forming polymers

Two monomers, one of which has a functionality of greater than two.



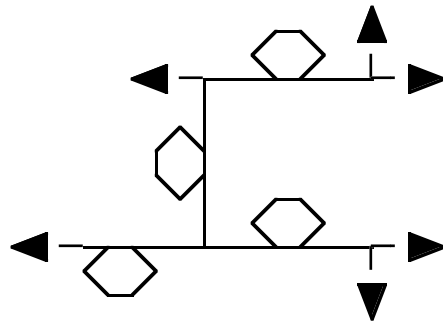
+



di functional
bicarboxylic acid

glycerol

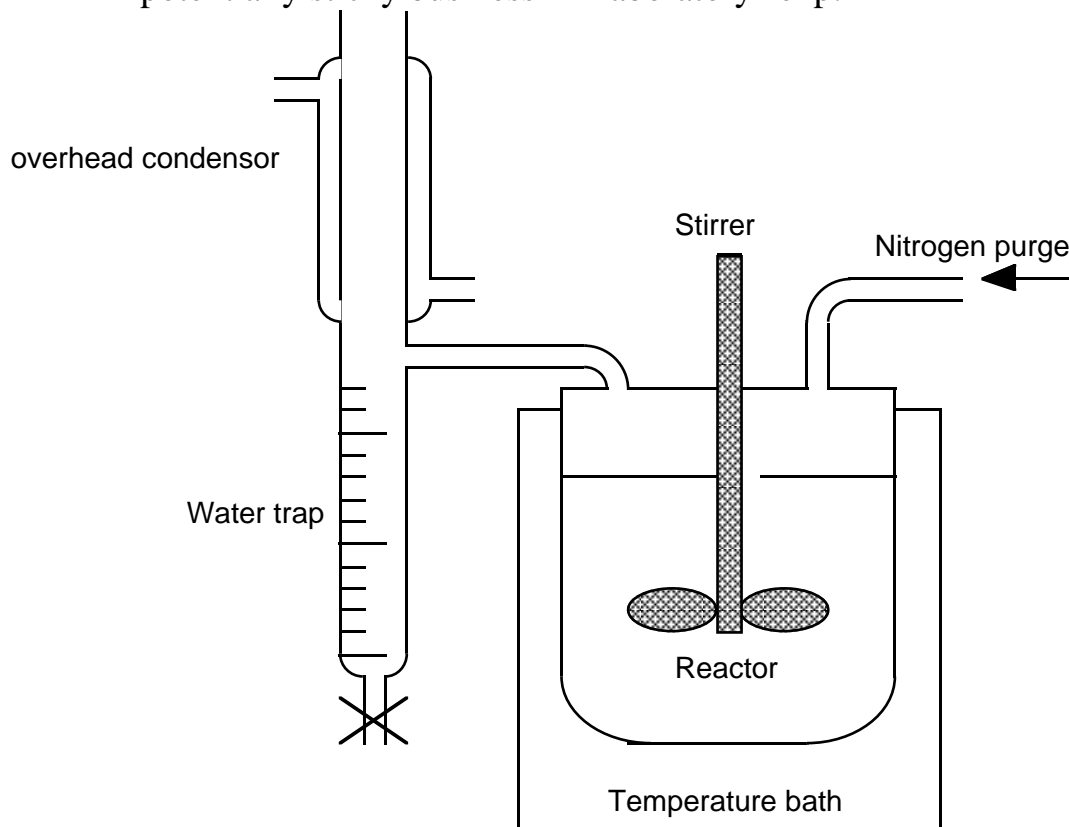
tri functional benzene



This is the basis for thermostat;
polyester resins.

3.2 Stepwise Polymerisation Kinetics of conversion and MMD

A potentially sticky business Laboratory exp:



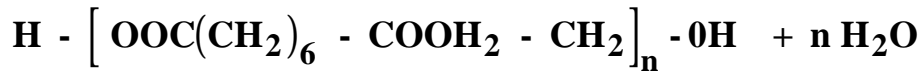
An example

Two di functional monomers A and B

A = ethylene glycol Conc C_A (kmol/m³)
HO-CH₂-CH₂-OH

B = Suberic acid C_B (kmol/m³)
HOOC-(CH₂)₆-COOH

Polymerises to form



Sequence

1. HO-A-OH, HOOC-B-COOH
 EG SA
2. HO-A-COO-B-COOH
3. HO-A-COO-B-COO-A-OH
4. HO-[A-COO-B]_n-COOH

Recipe

- a) Solution polymerisation (decalin) eases mixing and HT problems at end of reaction
- b) 1 mol acid, C_A
- c) N₂ purge, heat to 150°C
- d) 1 mol glycol, C_B
- e) React ~ 1 hr
- f) Reaction kinetics followed from time dependence of water evolution.

Analysis of kinetics.

Assume each esterification is independent of length of chain.

Rate of polymer formation $R = k[\text{C}_A] [\text{C}_B] [\text{C}_B]$

Last [C_B] is included as catalyst reaction

Equi molar C_A = C_B = C

Monomer kinetics $R = -k[\text{C}]^3$

Mass Balance on C, batch $\frac{d[\text{C}]}{dt} = -k[\text{C}]^3$

integrate

$$2kt = \frac{1}{[\text{C}]^2} - \frac{1}{[\text{C}_0]^2}$$

for boundary condition t = 0, C = C₀

Straight line plot $\frac{1}{C^2}$ vs t. shows assumption correct

Rate const k obeys simple temp dependence.

$$k = A e^{-E/RT}$$

Extent of Reaction P look at the ends!

Let original number of COOH groups be N_0
 " " " " " N at time t

Define extent of reaction as fraction reacted.

Defn
$$P = \frac{N_0 - N}{N_0} = 1 - \frac{N}{N_0}$$

Fraction of COOH groups not reacted
$$\frac{N}{N_0} = (1 - P)$$

3.3 Derivation of Molecular Mass moment \overline{DP}_n

Surprise! It is possible to derive \overline{M}_n without knowing full distribution.

Big surprise! Its easy!

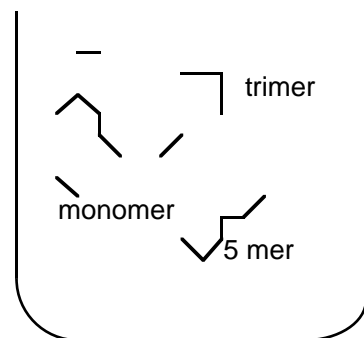
Consider single di functional monomer

Ex. HO-R-COOH

Sequence	1	HO-R-COOH	HO-R-COOH
	2	HO-R-COO-R-COOH	
	3	HO-R-COO-R-COO- COOH	
	n	HO-[R-COO] _n - COOH	

Degree of polymerisation r, 1, 2, 3, 4, 5

Number of chains with degree of polymerisation r, 3, 1, 0, 1, 1



$\sum N_r = 6$ total number of molecules in reaction pot (all sizes)

$\sum N_r r = 14$ total number of repeat units

Consider whole population, monomer and polymer

$$\text{Definition } \overline{DP}_n = \frac{\sum N_r r}{\sum N_r} = \frac{\text{original nos repeat units}}{\text{total nos of molecules at } = t}$$

$$= \frac{\text{original nos of COOH groups}}{\text{Nos COOH groups at time } t}$$

$$\overline{DP}_n = \frac{N_0}{N} = \frac{1}{[1 - P]}$$

Number Ave BP

Number Ave MM

$$\overline{DP}_n = \frac{1}{[1 - P]} \quad \overline{M}_n = \frac{M_0}{[1 - P]}$$

Extent of reaction, (range P= 0 - 1)

P = 0.9	$\overline{DP}_n = 10$
P = 0.99	= 100
P = 0.999	= 1,000 Polymer

Very high conversions are required in order to obtain a significant Molecular Mass.

Immediate significance to reactor design.

Batch, or genuine plug flow

Single CST a dead dog

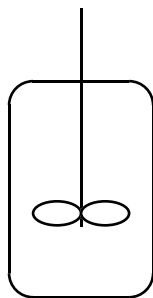
Commercial batch 10 - 20 tonne

Batch STR

a) Melt polymerisation

Liquid monomer → Liquid polymer

Low viscosity	High viscosity
10^{-3} Pas	10^3 Pas

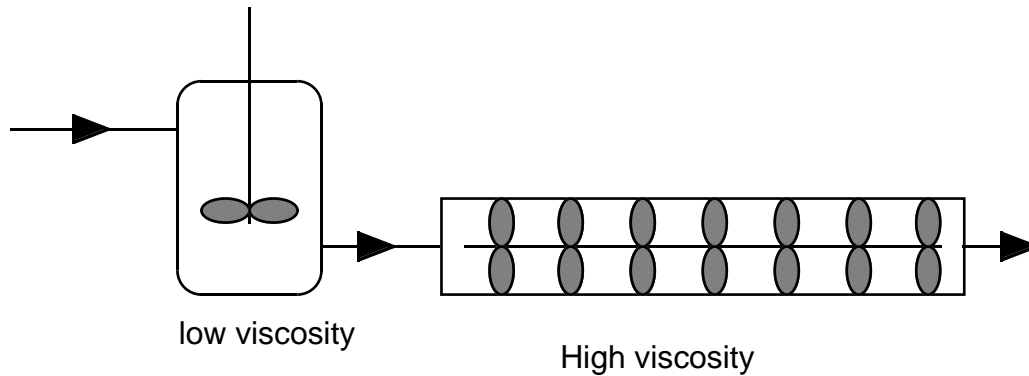


HT and mixing difficulties Exothermic, so go slow → low temps
120°C

Typical cycle time 8 - 20 hrs

- b) Solution polymerisation**
 eases mixing and HT problems
 but cost penalty → subsequent
 polymer solvent separation

c) Continuous reactor



3.4 Derivation of the full MMD

Its deceptively easy!

Because rate constant k is independent of chain length we can
 apply probability
 arguments.

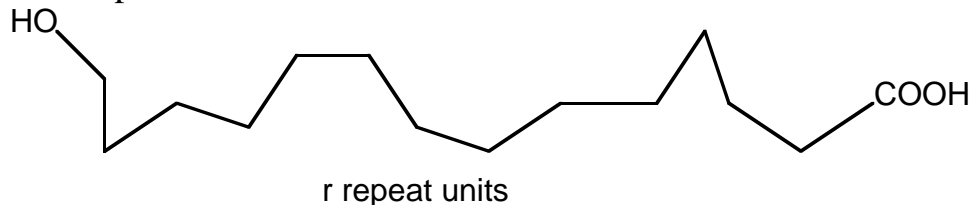
Consider single species, di functional monomer CO-R-COOH

For extent of reaction P

Prob that a COOH group has reacted = P
 " " " " not " = $(1 - P)$

For extent of reaction P , pick up a chain at random.

What is prob that it is an r mer?



For molecule to be an r mer it must have, $r - 1$ reacted COOH groups
 and one reacted COOH group.

$$\begin{aligned} \text{Prob of } r \text{ mer} &= \text{Prob } (r - 1) \text{ groups} \times \text{Prob of one unreacted groups} \\ &= P^{(r - 1)} (1 - P) \end{aligned}$$

Assume nos frac of r mers $x_r = \text{Prob of } r \text{ mer}$

$$\text{Then } x_r = p^{(r - 1)} (1 - P)$$

$$\text{Equivalently } \left[x_m = p^{\left(\frac{m}{m_0} - 1\right)} (1 - P) \right]$$

$$x_r = \frac{N_r}{\sum N_r} = \frac{N_r}{N} = P^{(r - 1)} (1 - P)$$

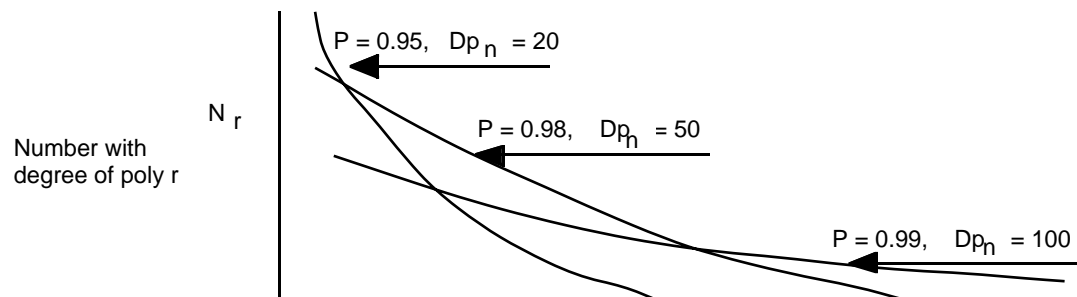
N = Total nos of molecules, all sizes
 = " " " COOH groups at time t

$$\frac{N}{N_0} = (1 - P) \quad N = N_0(1 - P) = \text{Defn of } P!$$

So

$$N_r = N_0 p^{(r - 1)} (1 - p)^2 \quad \text{Big equation!}$$

So we now know full distribution in terms of extent of conversion P .



3.5 Derive \overline{DP}_n , the number average degree of polymerisation from full distribution.

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

N_r = number of chains with degree of polymerisation r

N_0 = number of origin monomer repeat units.

P = extent of reaction.

Also

$$\sum_{r=1}^{\infty} N_r = N = N_0(1 - P)$$

By Defn

$$\overline{DP}_n = \frac{\sum_{r=1}^{\infty} N_r r}{\sum_{r=1}^{\infty} N_r} = \frac{N_0(1 - P)^2}{N_0(1 - P)} \sum_{r=1}^{\infty} rP^{(r-1)}$$

$$\overline{DP}_n = (1 - P) \sum_{r=1}^{\infty} rP^{(r-1)} = (1 - P)(1 + 2P + 3P^2 + \dots)$$

we need to determine this summation.

Known fact

For $P < 1$ $\sum_{r=0}^{\infty} P^r = \frac{1}{(1 - P)}$ Binomial expansion

Rework our summation

$$\overline{DP}_n = (1 - P) \sum_{r=1}^{\infty} rP^{(r-1)}$$

Now $\frac{\partial}{\partial P} \sum_{r=0}^{\infty} P^r = \sum_{r=1}^{\infty} rP^{(r-1)}$

So
$$\begin{aligned} \overline{DP}_n &= (1 - P) \frac{\partial \sum P^r}{\partial P} \\ &= (1 - P) \frac{\partial}{\partial P} \frac{1}{(1 - P)} \end{aligned}$$

$$= (1 - P) \frac{1}{(1 - P)^2}$$

$$\overline{DP}_n = \frac{1}{(1 - P)} \quad \text{As before "that's lucky!"}$$

3.6 Derive an expression for \overline{DP}_w , weight average degree of polymerisation.

By defn
$$\overline{DP}_w = \frac{\sum N_r r^2}{\sum N_r r}$$

$$= \frac{\sum r^2 P^{r-1}}{\sum r P^{r-1}}$$

From previous calc.
$$\sum r P^{r-1} = \frac{1}{(1 - P)^2}$$

determine
$$\sum r^2 P^{(r-1)}$$

$$\begin{aligned} \sum r^2 P^{(r-1)} &= \frac{\partial}{\partial P} \sum r P^r = \frac{\partial}{\partial P} P \sum r P^{r-1} \\ &= \frac{\partial}{\partial P} P / (1 - P)^2 \end{aligned}$$

So

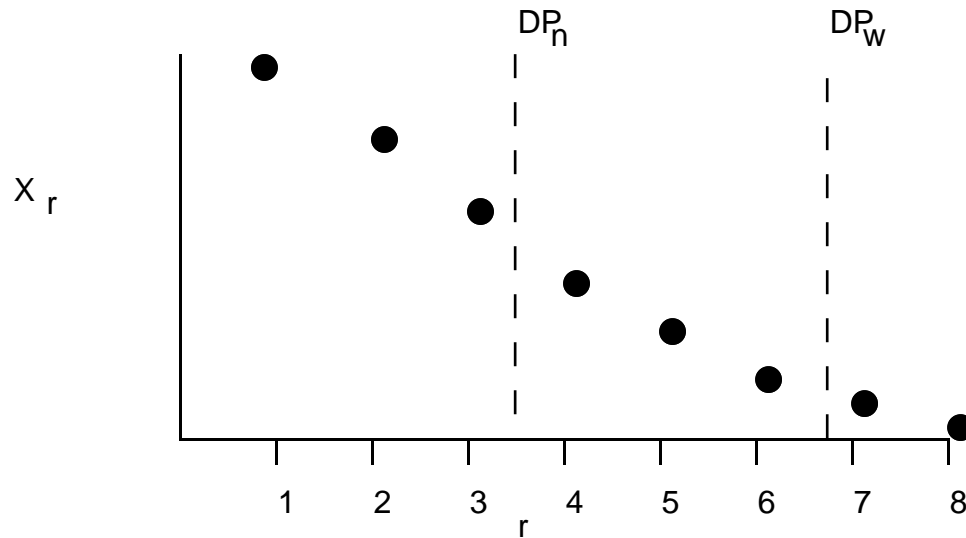
$$\begin{aligned} \overline{DP}_w &= (1 - P)^2 \frac{\partial}{\partial P} \left(P / (1 - P)^2 \right) \\ &= (1 - P)^2 \frac{(1 + P)}{(1 - P)^3} \end{aligned}$$

$$\overline{DP}_w = \frac{(1 + P)}{(1 - P)}$$

$$\overline{M}_w = M_0 \frac{(1 + P)}{(1 - P)}$$

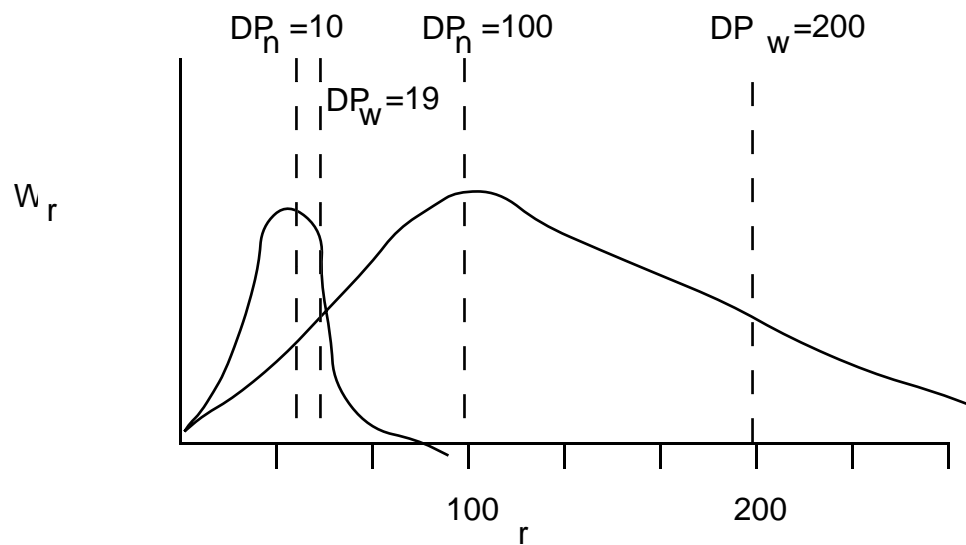
Nos fraction plots x_r x_m

$$x_r = \frac{N_r}{\sum N_r} = \frac{N_0(1 - P)^2 P^{r-1}}{N_0(1 - P)} = (1 - P)P^{r-1}$$



Weight fraction plots

$$w_r = \frac{N_r r}{\sum N_r r} = \frac{N_0 P^{r-1} (1 - P)^2 r}{N_0} = (1 - P)^2 P^{r-1} r$$



Polydispersity

$$\frac{\overline{DP}_w}{\overline{DP}_n} = \frac{(1 + P)}{1 - P} (1 - P) = 1 + P$$

Limit, when P approaches 1, then Polydispersity = 2 max polydispersity for stepwise polymerisation

3.6 Molecular mass control in stepwise polymerisation

Usually we are struggling to get high MMs with stepwise polymerisation; however if $P = 1$ for stoichiometric mix, no chain ends exist! → trouble!

Non stoichiometric mixtures of monomers. Consider two monomer system.

Cost:-	HOOC-A-COOH Type A monomer	HO-B'-OH Type B monomer
--------	-------------------------------	----------------------------

Strategy - chain end counting

At start $t = 0$

Let N_o^A be original nos end groups (COOH) on type A monomers

" N_o^B " " " end groups (OH) on type B monomers

Let $q = \frac{N_o^A}{N_o^B}$ where $q < 1$

$$\begin{aligned} \text{Total nos of molecules at } t=0 &= \frac{1}{2} [N_o^A + N_o^B] \\ &= \frac{N_o^A}{2} \left(1 + \frac{1}{q} \right) \end{aligned}$$

(This equals total nos of repeat units at $t = 0$)

At time t .

When for species of type A extent of reaction is P
then " " " B " " Pq

$$\left[P_A = \frac{N_o^A - N^A}{N_o^A}, \quad P_B = \frac{N_o^B - N^B}{N_o^B}, \quad N_o^A - N^A = N_o^B - N^B \right.$$

When extent of reaction is P.

number of A end groups not reacted $= N_o^A (1 - P)$

number of B " " " " = $N_0^B(1 - Pq)$
 number of chain ends = number of unreacted groups

$$= N_0^A(1 - P) + N_0^B(1 - Pq)$$

$$= N_0^A \left\{ (1 - P) + \left(\frac{1}{q} - P \right) \right\}$$

number of molecules (all sizes)

$$= \frac{N_0^A}{2} \left\{ (1 - P) + \left(\frac{1}{q} - P \right) \right\}$$

each molecule has two ends!

By definition

$$\overline{DP}_n = \frac{\sum N_r r}{\sum N_r} = \frac{\text{total nos repeat units}}{\text{total nos molecules}}$$

$$= \frac{\frac{N_0^A}{2} \left[1 + \frac{1}{q} \right]}{\frac{N_0^A}{2} \left\{ (1 - P) + \left(\frac{1}{q} - P \right) \right\}}$$

$$\overline{DP}_n = \frac{1 + q}{1 + q(1 - 2P)}$$

$$\text{As } P \rightarrow 1 \quad \frac{Lt}{P \rightarrow 1} \quad \overline{DP}_n = \frac{1 + q}{1 - q}$$

Ex. let $q = \frac{100}{101}$ ie, 1% diff. limiting $\overline{DP}_n = 200$

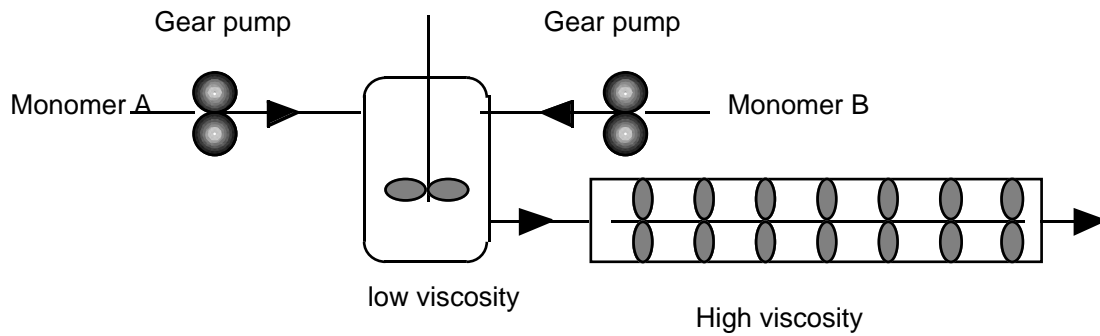
Stoichiometric

$$\overline{DP}_n = \infty$$

Results tell us

1) For high \overline{DP}_n near stoichiometric monomer balance necessary.

Difficult to achieve in continuous flows.



- 2) In "theory" we could control \overline{DP}_n by control relative feed rate of monomers, but generally not practical.

3.8 Commercially viable method of MM control

Add stabiliser - mono functional species

General species $R'COOH$

(Carboxylic acid)

Example add CH_3COOH to Nylon
(acetic acid)

Yields $R'COO-(RCOO)_n RCOOH$

Dead end! - ensures we have some ends even if $P = 1$

Works for Single di function monomer or two di functional monomers

(see 89 Tripos) - big challenge

Example, Consider single monomer of type $HO-R-COOH$

Strategy chain end counting (again!)

At start $t = 0$

N_o monomer molecules of type $HO-R-COOH$

N_o^s stabiliser molecules of type $R'COOH$

$$\text{define, } q = \frac{N_o^s}{N_o} < 1$$

$$\begin{aligned} \text{Total number of molecules at } t = 0 &= N_o + N_o^s \\ &= N_o[1 + q] \end{aligned}$$

$$\text{Sum of all starting molecules} \quad \sum N_r \quad r = N_o[1 + q]$$

At time t , extent of reaction is P .

Fraction of reacted OH groups = P

\therefore Number of reacted " " = $N_o P$

and " " " COOH " = $N_o P$
 (i.e, the same)

∴ Number of unreacted COOH groups
 $= (N_o + N_o^s) - N_o P$

This must be equal to the total number of molecules present as unreacted monomer, stabiliser and polymer all have one COOH group.

So $\overline{DP}_n = \frac{\sum N_r r}{\sum N_r} = \frac{N_o(1 + q)}{(N_o + N_o^s - N_o P)}$
 $= \frac{1 + q}{q + (1 - P)}$

Lt $p \rightarrow 1$, $\overline{DP}_n = \frac{1 + q}{q}$

Let $q = 0.1$ $\overline{DP}_n = 11$

$q = 0.01$ $\overline{DP}_n = 101$

$q = 10^{-3}$ $\overline{DP}_n = 1001$ a useful result.

Add a bit of mono functional species - ensures you won't block up reactor forming no chain ends (single molecule!)

3.7 The time evolution of MM distribution

We have derived N_r as a function of P.

" now derive P as a function of t (easy).

Hence determine N_r as a function of t.

Consider monomer HORCOOH

N_o = original number of COOH groups

N = " " " " at time t and state P

Extent of reaction

Polymerisation $P = \frac{N_o - N}{N_o}$, $N = N_o(1 - P)$

Concentration of monomer [C] $[c]/[c_o] = N / N_o = (1 - P)$

Kinetics, (plausibility), Batch

$$\frac{d[c]}{dt} = k[c][c] = k[c]^2$$

at $t = 0$. $N = N_0$, $[c] = [c_0]$.

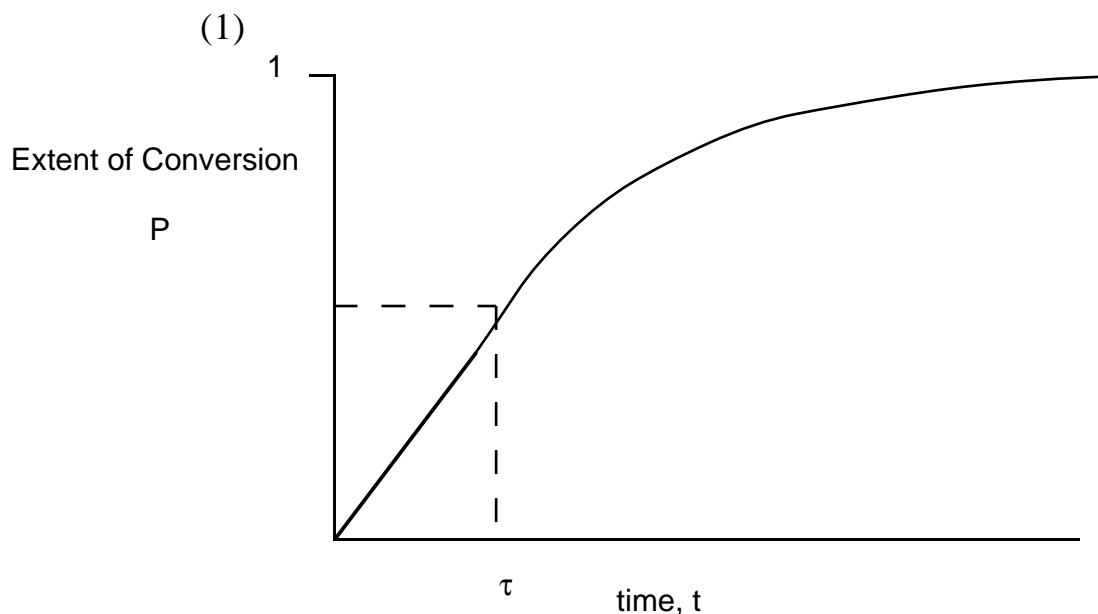
at $t = t$, $N = N$, $[c] = [c] = c_0(1 - P)$

$$\int_{c_0}^{c_0(1-P)} -\frac{dc}{c^2} = k \int_0^t dt$$

$$\frac{1}{c_0(1-P)} - \frac{1}{c_0} = kt$$

So, Extent of Reaction

$$P = \frac{k c_0 t}{1 + k c_0 t}$$



Variation of extent of reaction with time.

Polymerisation initially has linear kinetics.

Time const. $\tau = \frac{1}{kC_0}$

But note slow approach to $P = 1$.

Result

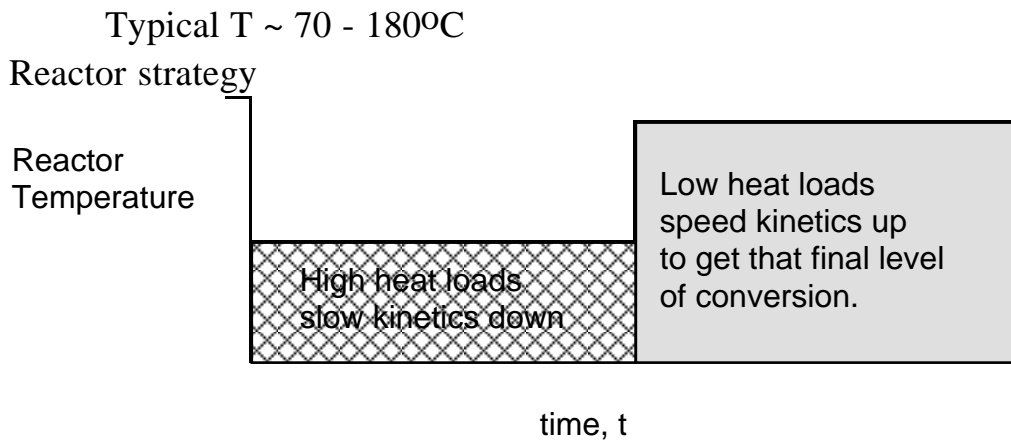
Early times - large changes \rightarrow exothermic reaction \rightarrow heat loads greatest - good news. Viscosity is low.

In order to get sig MW. $P \rightarrow 1$. reaction time is $\gg \tau$.

If $\tau = 100\text{s}$ $RT \simeq 8 \text{ hrs,}$ for $P = 0.99.$

Temp dependence.

$k = Ae^{-E/RT}$ Often reaction is exothermic.
 increase reaction temperature. T K increases and τ decreases
 " " " faster polymerisation.
 But limitation; heat loads and high temperature side reactions.



From a previous lecture

$$N_r = N_0 P^{r-1} (1 - P)^2$$

(2)

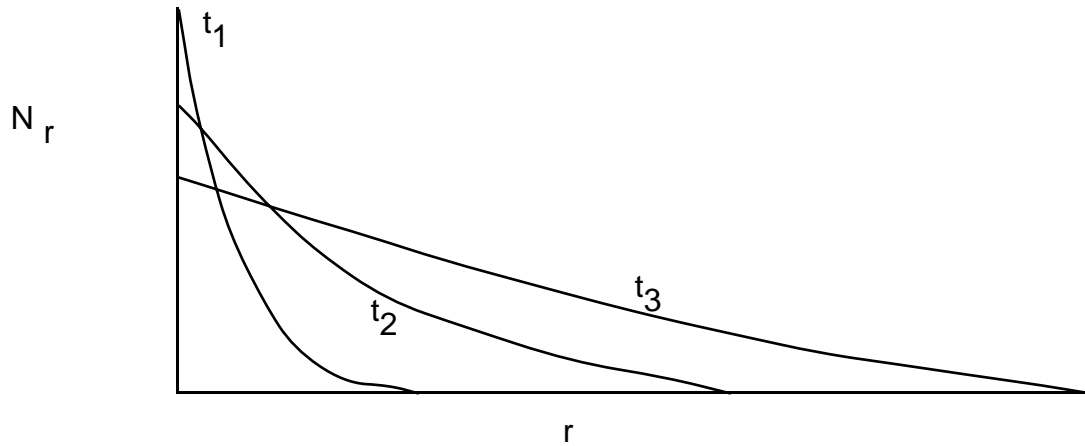
Combine (1) and (2)

$$N_r = \left[\frac{k c_0 t}{1 + k c_0 t} \right]^{r-1} \left[1 - \frac{k c_0 t}{1 + k c_0 t} \right]^2$$

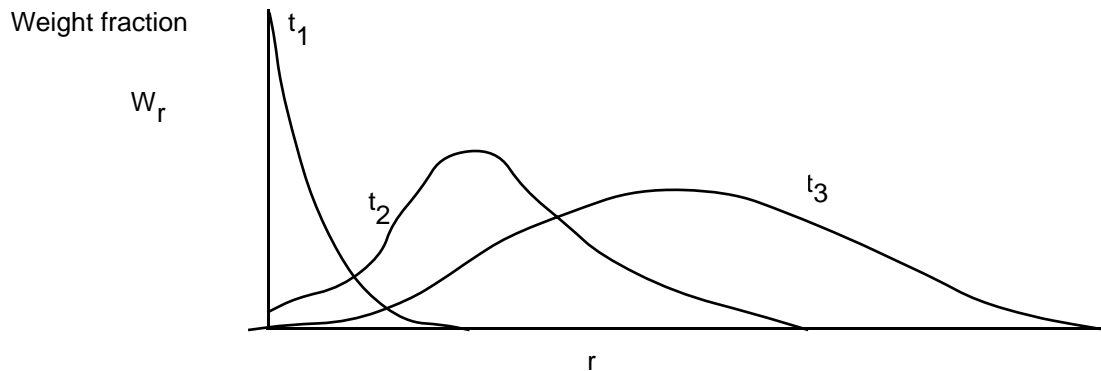
$$= \frac{N_0 k^{r-1} c_0^{r-1} t^{r-1}}{(1 + k c_0 t)^{r+1}} \quad \text{which gives } N_r \text{ as a}$$

function of t.

Number plot



weight fraction plot



We now know time dependence for.

- A) Conversion (standard kinetics)
- B) Molecular mass evolution (this is new)

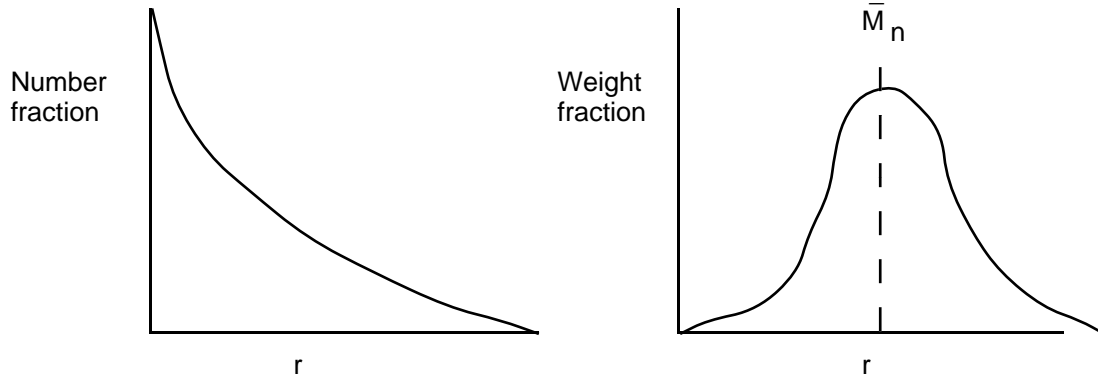
3.10 Summary (things you should know!)

Stepwise polymerisation

- 1) MM distribution controlled by P the extent of reaction.
Time changes both conversion and MM distribution.
- 2) $P > 0.95$ for significant MM.
- 3) When $P > 0.9$ $\frac{M_w}{M_n} \sim 2$

derivation $\frac{\partial}{\partial \mathbf{P}} \sum_0^{\infty} \mathbf{P}^r = \sum_1^{\infty} r \mathbf{P}^{(r-1)}$

4) Typically



Peak in w_M occurs near \bar{m}_n (not proved in lectures - but you can do this!)

5. Increase. in T, increases kinetics

Possible T profile

Stage 1 low temp → most heat load

Stage 2 high " → faster kinetics
low heat load

6. MM control:- Prevent the single molecule!

a) two di functional monomers. non stoichiometric

balance

b) Add mono functional stabiliser

