STATISTICS OF LINEAR POLYCONDENSATION

TYPICAL REACTIONS

Students - ugh !

Attributed to Mark Twain
- there are lies, damn lies, and statistics

STATISTICS OF LINEAR POLYCONDENSATION

KEY ASSUMPTION

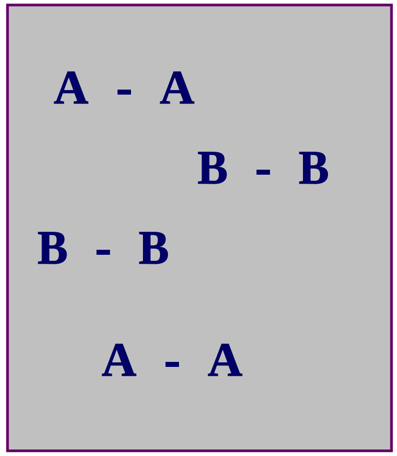
Reaction rate independent of molecular size

DEFINITION

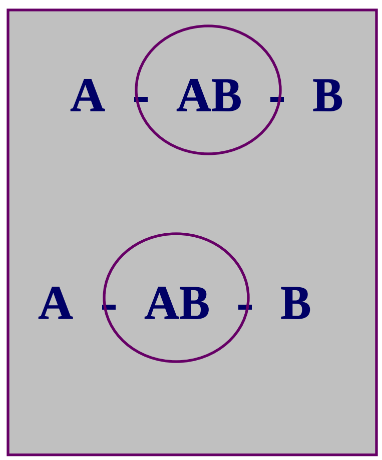
The extent of reaction p is also the probability that a functional group has reacted (at some time t)

DEFINITION OF p AS A PROBABILITY

AT TIME t = 0



AFTER A TIME t



What is the probability that a group, taken at random, has reacted ?

If 50% of the "B" groups have reacted, then the probability that a "B", taken at random, has reacted = 0.5

STATISTICS OF LINEAR POLYCONDENSATION

The Number Average Degree of Polymerization

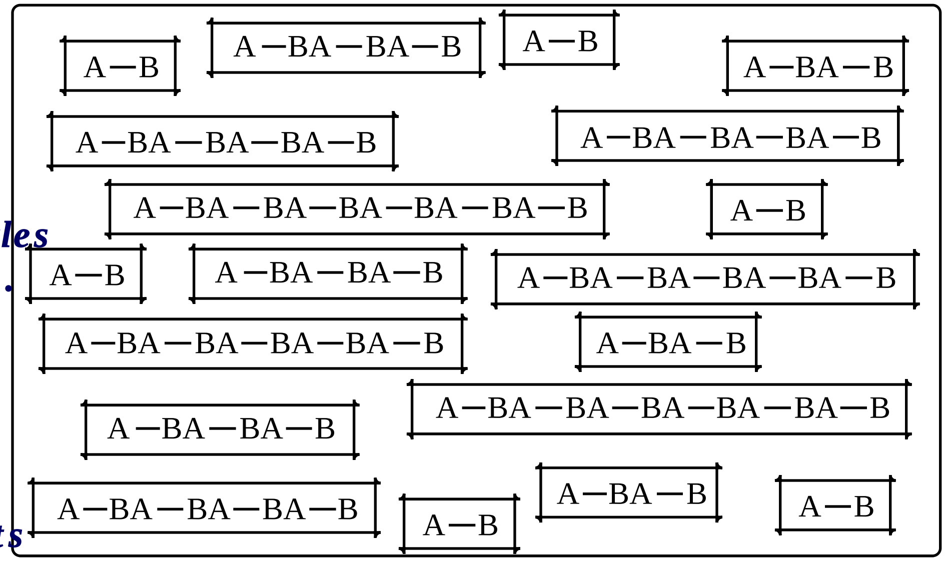
Two types of linear polycondensations:

A—B + A—B ⇌ A—BA—B (Type I)

In Type I we can count the number of molecules present bycounting the number of end groups.

A—A + B—B ⇌ A—AB—B (Type II)

Also true for Type II providing we start with exactly equal equivalents of the two reactants.



Definition: The Number Average Degree of Polymerization

$$\bar{x}_n = \frac{\text{Total Number of Molecules Originally Present (Monomers)}}{\text{Total Number of Molecules in the System After the Polymerization has Stopped}} = \frac{N_0}{N}$$

STATISTICS OF LINEAR POLYCONDENSATION

Definition: p is the fraction of functional groups that have reacted
or: p is the probability that one such group taken at random has reacted

We can express $\bar{x}_n$ in terms of the conversion p by recalling that:

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

The number of molecules (N, N_0) can simply be converted to concentrations (c, c_0) so that:

$$\bar{x}_n = \frac{N_0}{N} = \frac{c_0}{c} = \frac{1}{(1 - p)}$$

The Number Average Molecular Weight, $\bar{M}_n$ is simply:

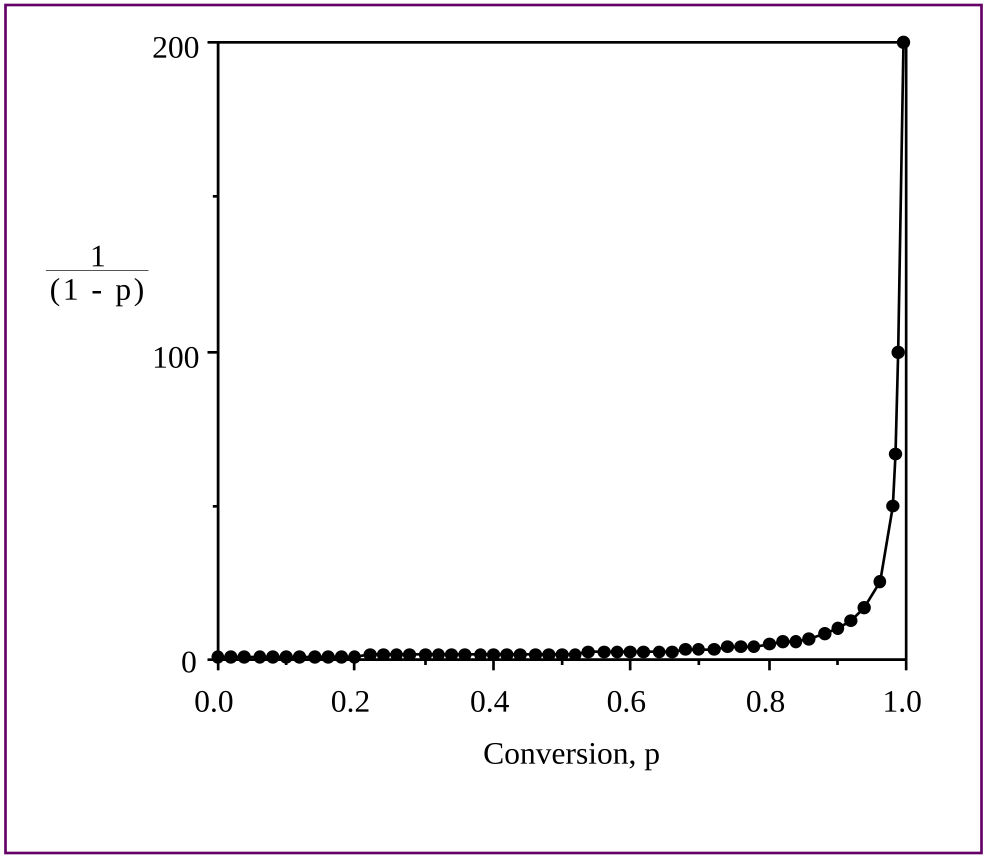
$$M_n = M_0 x_n = \frac{M_0}{(1 - p)}$$

Careful !
For Type II polycondensations we must define a mean molecular weight, M_0 , for the structural unit

STATISTICS OF LINEAR POLYCONDENSATION

The Number Average Degree of Polymerization as a Function of Conversion

Remember: $\bar{x}_n = \dfrac{1}{(1 - p)}$



RAMIFICATIONS:

- ***High molecular weight is only achieved at very high degrees of conversion.***

- ***At 90% conversion (p = 0.90) the number average degree of polymerization is only 10 ! Equivalent to number average molecular weight of ≈ 1000 g/mole.***

- ***At 95% conversion (p = 0.95) the number average degree of polymerization is only 20 ! Equivalent to number average molecular weight of ≈ 2000 g/mole.***

- ***Need to have conversions of 99.5% to obtain molecular weights in the range of 20,000 g/mole***

- ***An industrial nightmare !***

THE EFFECT OF NON-STOICHIOMETRIC EQUIVALENCE OF THE BIFUNCTIONAL MONOMERS

Type II Polycondesation: A—A and B—B

Let N_0 be the number of monomers we start with

N be the number of chains after a fraction of p groups has reacted N_B

N_A be the number of A groups

N_B be the number of B groups (present in excess of A)

$$r = \frac{N_A}{N_B}$$

$$\bar{x}_n = \frac{N_0}{N} = \frac{1 + r}{1 + r - 2rp}$$

(see page 82 for details)

Theoretical Limit:

$$\bar{x}_n = \frac{1 + r}{1 - r} \quad \text{as } p \rightarrow 1 \text{ (complete reaction)}$$

A 1% excess of B (ie r = 0.99) means that the upper limit for the number average degree of polymerization is 199.

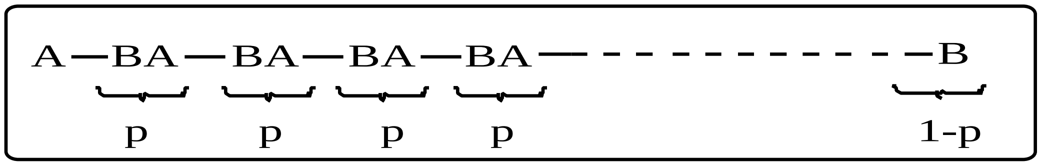
To obtain high molecular weight polymer great care must be taken to make sure that there are equal amounts of monomer at the start of the reaction, that these monomers are pure and that one of these monomers does not get lost in preference to the other.

MOLECULAR WEIGHT DISTRIBUTIONS IN LINEAR CONDENSATION POLYMERS

Type I Polycondesation: A—B

Question: What is the probability that a molecule selected at random from the mixture of polymerizing chains, where the extent of reaction is p, is an x-mer ?

Definition: x-mer — a molecule containing x units in its chain



Hence: the probability that the molecule has exactly x units, P_x , is:

$$P_x = (1-p)\,p^{(x-1)}$$

MOLE FRACTION DISTRIBUTION OF X-MERS

The probability of finding an x-mer at random must be equal to the mole fraction of x-mers present:

$$\frac{N_x}{N} = X_x = (1-p)\,p^{(x-1)}$$

N_x is the number of x-mers present in the pot
N is the total number of molecules at p
X_x is the mole fraction of x-mers

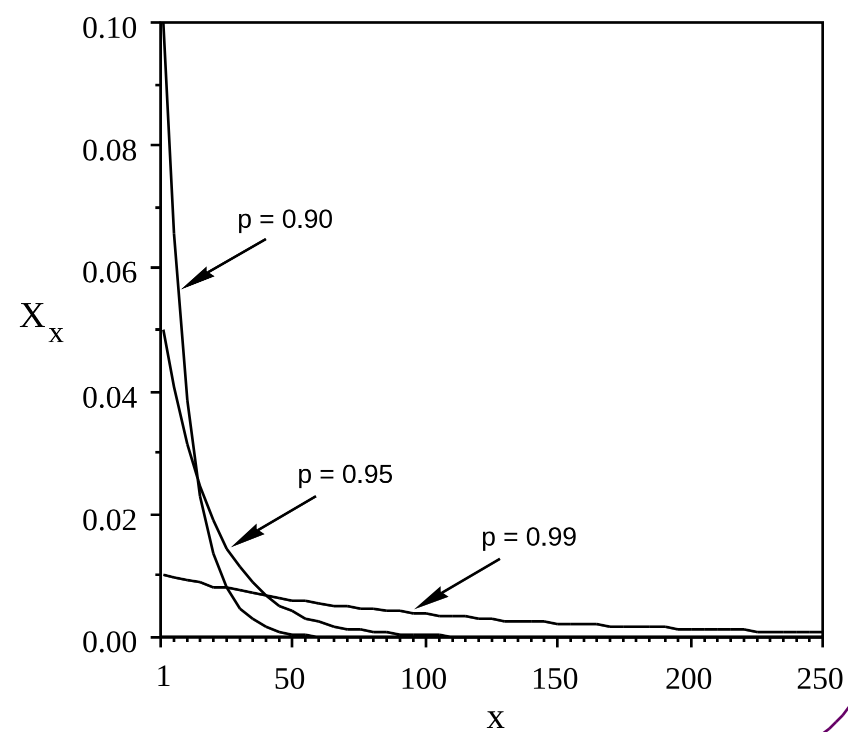
An alternative way of expressing the same thing is:

The Number Distribution Function

but in terms of N_0 rather than N.

$$\bar{x}_n = \frac{N_0}{N} = \frac{1}{(1-p)} \quad \text{or } N = N_0(1-p)$$

$$N_x = N_0 (1-p)^2\, p^{(x-1)}$$



Mole fraction distribution of x-mers

Note: there are always a larger *number* of monomers present than any other species, regardless of the extent of reaction !!

WEIGHT FRACTION DISTRIBUTION OF X-MERS

The weight fraction of x-mers present in the pot after an extent of reaction p is:

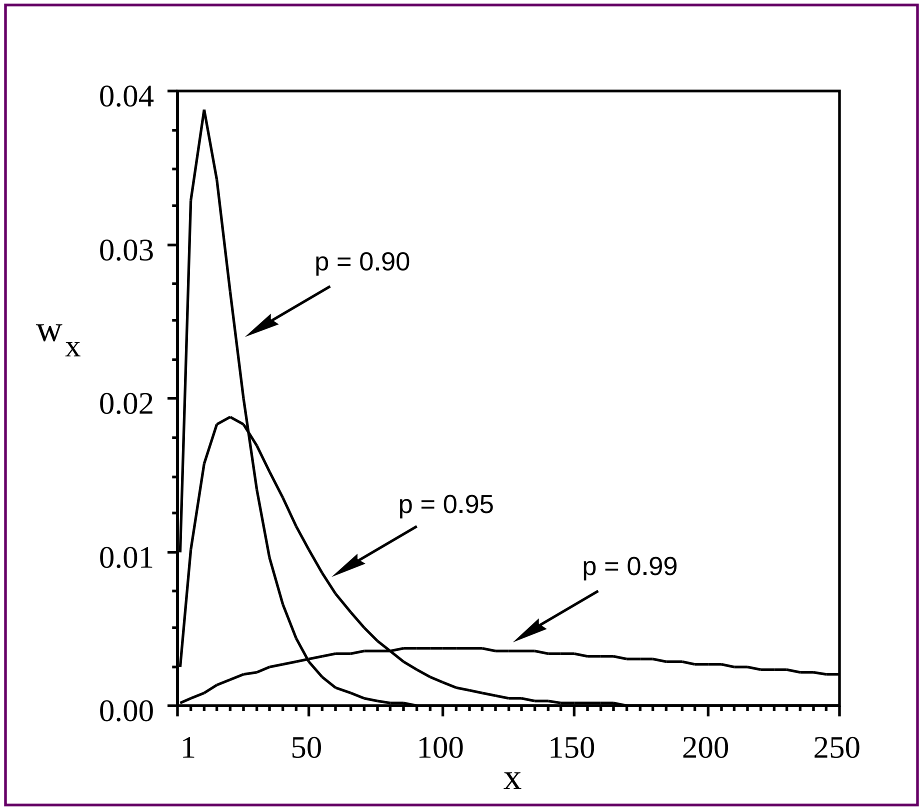
$$w_x = \frac{\text{weight of all x-mers}}{\text{weight of all units}} = \frac{x N_x M_0}{N_0 M_0}$$

Substituting in the previous equation:

$$N_x = N_0 (1 - p)^2 p^{(x - 1)}$$

Leads to the *Weight Fraction Distribution*:

$$w_x = x(1 - p)^2 p^{(x - 1)}$$



Weight fraction distribution of x-mers

Note: there is a maximum in this distribution that shifts to higher values as p increases.

THE MOST PROBABLE DISTRIBUTION AND POLYDISPERSITY

It follows that the *Number Average Degree of Polymerization* must be the sum of the product of the *Mole Fraction of x-mers* times *x*, the number of units in the x-mer.

$$\bar{x}_n = \sum x X_x = \sum x p^{(x-1)} (1-p)$$

Because p < 1 we can use the series convergence .

$$\sum x p^{(x-1)} = \frac{1}{(1-p)^2}$$

Hence:

$$\bar{x}_n = \frac{1}{(1-p)}$$

Similarly:

$$\bar{x}_w = \sum x w_x = \sum x^2 p^{(x-1)} (1-p)^2$$

And: $\sum x^2 p^{(x-1)} = \frac{(1+p)}{(1-p)^3}$

Hence:

$$\bar{x}_w = \frac{(1+p)}{(1-p)}$$

Polydispersity

A Measure of the Breadth of the Distribution defined as:

$$\frac{\bar{x}_w}{\bar{x}_n} = (1+p) \quad \text{As } p \rightarrow 1 \quad \frac{\bar{x}_w}{\bar{x}_n} = 2$$