STATISTICS OF LINEAR POLYCONDENSATION

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The Number Average Degree of Polymerization

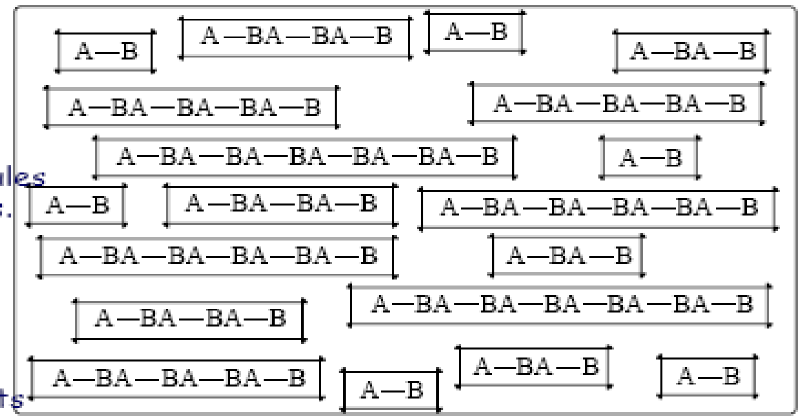
Two types of linear polycondensations:

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:

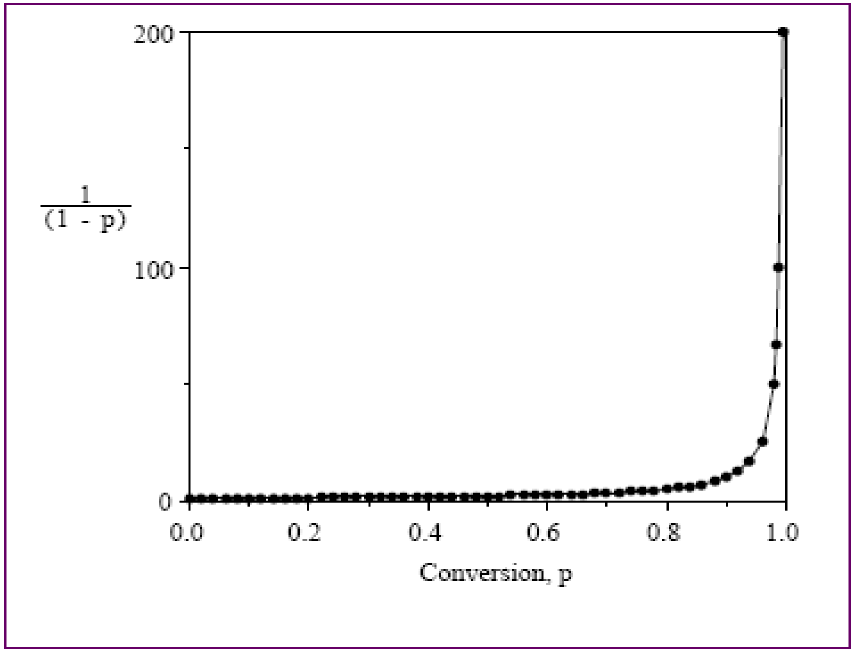
$$M_n = M_0 x_n = \frac{M_0}{(1 - p)}$$

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



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.

Problem What feed ratio of hexamethylene diamine and adipic acid should be employed in order to obtain a polyamide of $\overline{M}_n = 10{,}000$ at 99% conversion ? Identify the end groups of this product.

Answer:

Formula weight of repeating unit $-[HN(CH_2)_6NHCO(CH_2)_4CO]- \;=\; 226$

$M_0 = \frac{1}{2} \times 226 = 113; \; \overline{X}_n = \overline{M}_n/M_0 = 10{,}000/113 = 88.5$

with $p = 0.99$

$$\overline{X}_n = \frac{1 + r}{1 + r - 2r(0.99)} = 88.5 \qquad \text{Solving, } r = 0.9974$$

The polymerization is carried out with either $COOH/NH_2$ or $NH_2/COOH = 0.9974$. For $COOH/NH_2 = 0.9974$, all end groups will be NH_2; for $NH_2/COOH = 0.9974$, all end groups will be COOH.

$$\overline{X}_n = \frac{N_0}{N} = \frac{1 + r}{1 - r}$$

$$\overline{X}_w = \frac{4}{1 - r} - \frac{4}{1 + r} + \frac{1 - r}{1 + r}$$

$$\frac{\overline{X}_w}{\overline{X}_n} = \frac{4}{1 + r} - \frac{4(1 - r)}{(1 + r)^2} + \left(\frac{1 - r}{1 + r}\right)^2$$

Problem A polyester, poly(ethylene terephthalate), was synthesised by reacting one mole of dimethyl terephthalate and two moles of ethylene glycol, the reaction being carried to 100% exchange of the methyl group forming the ester link between glycol and terephthalate. Calculate (a) number average degree of polymerization, (b) weight-average degree of polymerization, (c) polydispersity index of the product,

Answer:

Consider A = $-COOCH_3$, B = $-OH$. Therefore, for the given composition, $r = \frac{1}{2}$

$$\overline{X}_n = (1 + \tfrac{1}{2})/(1 - \tfrac{1}{2}) = 3$$

(b)
$$\overline{X}_w = \frac{4}{1 - \frac{1}{2}} - \frac{4}{1 + \frac{1}{2}} + \frac{1 - \frac{1}{2}}{1 + \frac{1}{2}} = \frac{17}{3}$$

(c) $\overline{X}_w/\overline{X}_n = 17/9$

Molecular Weight Distribution (MWD)

Consider, as an example, an A—B type polymerization

$$x\,\mathrm{HO{-}R{-}COOH} \longrightarrow \mathrm{H{+}O\text{-}R\text{-}CO{+}_xOH} + (x-1)\,H_2O$$

The polymer chain may be written as (Ghosh, 1990):

$$\underset{1}{\mathrm{HO\text{-}R\text{-}COO}}\text{-}\underset{2}{\mathrm{R\text{-}COO}}\text{-}\underset{3}{\mathrm{R\text{-}COO}}\text{-}\underset{4}{\mathrm{R\text{-}COO}}\text{-}\cdots\cdots\ \underset{x}{\mathrm{R\text{-}COO\text{-}H}}$$

(III)

Probability that a given group has reacted = fractional extent of reaction (p).

Probability that a given group has not reacted = $1 - p$

In a polymer consisting of x monomer residues, the number of ester linkages = $(x - 1)$

Probability that the molecule contains $(x - 1)$ ester groups = p^{x-1}

Probability that the xth carboxyl group is unreacted = $(1 - p)$

Therefore, the probability that the molecule in question is composed of exactly x units = $p^{x-1}(1 - p) = n_x$

where n_x is the mole or number fraction of molecules in the polymer mixture which are x-mers, and is also given by

$$n_x = N_x/N$$

Here N_x is the number of molecules which are x-mers and N is the total number of molecules at the extent of reaction p. However, $N = N_0(1-p)$,

Equation therefore becomes

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

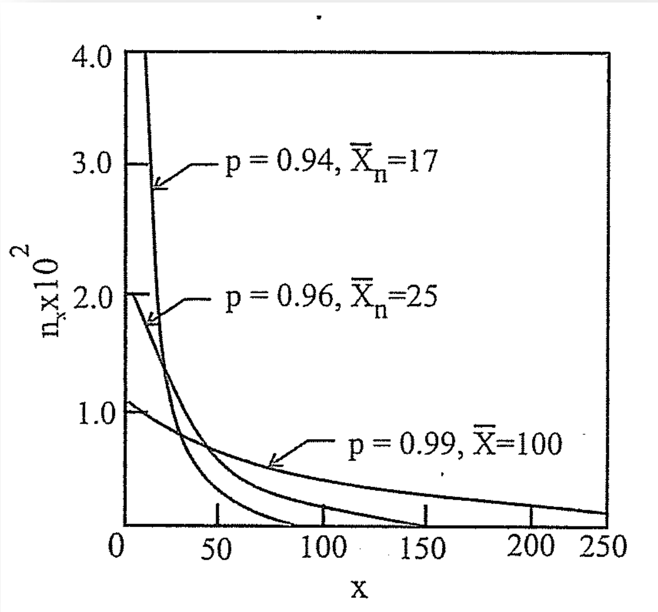
Total weight of all molecules $= N_0 M_0$ (neglecting unreacted ends OH and H).

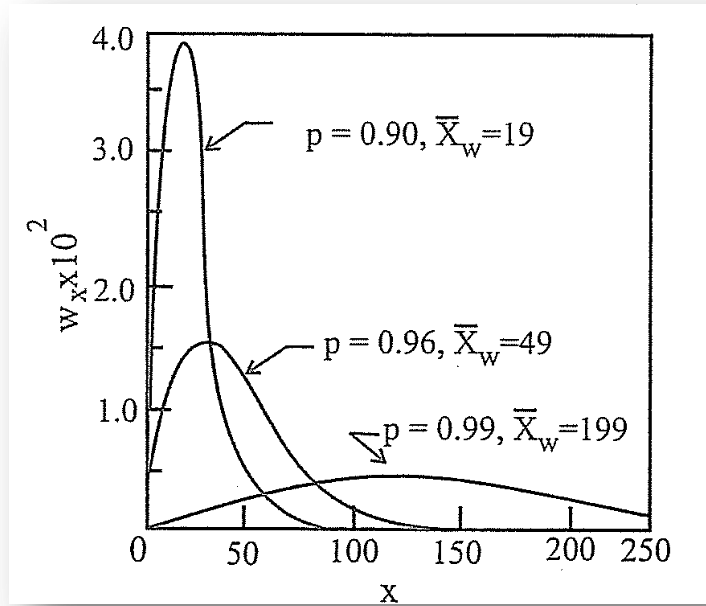
Hence the weight fraction w_x of x-mers is

$$w_x = \frac{N_x x M_0}{N_0 M_0} = \frac{N_x x}{N_0}$$

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

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


4.0
3.0
2.0
1.0
$n_x x10^2$
p = 0.94, $\overline{X}_n$=17
p = 0.96, $\overline{X}_n$=25
p = 0.99, $\overline{X}$=100
0 50 100 150 200 250
x


4.0
3.0
2.0
1.0
$w_x x10^2$
p = 0.90, $\overline{X}_w$=19
p = 0.96, $\overline{X}_w$=49
p = 0.99, $\overline{X}_w$=199
0 50 100 150 200 250
x

$$\overline{X}_n = \sum x n_x$$

$$\overline{X}_n = \sum x p^{x-1} (1 - p)$$

$$\overline{X}_n = (1 - p) \sum_{x=1}^{\infty} x p^{x-1} = \frac{1 - p}{(1 - p)^2} = \frac{1}{1 - p}$$

$$\overline{X}_w = \sum x w_x$$

$$\overline{X}_w = \sum x^2 p^{x-1} (1 - p)^2$$

$$\overline{X}_w = (1 - p)^2 \sum x^2 p^{x-1} = \frac{(1 - p)^2 (1 + p)}{(1 - p)^3} = \frac{(1 + p)}{(1 - p)}$$

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{\overline{X}_w}{\overline{X}_n} = (1 + p)$$

Problem In a polymerization of $H_2N(CH_2)_{10}COOH$ to form nylon-11, 95% of the functional groups is known to have reacted. Calculate (a) amount of monomer (in terms of weight fraction) remaining in the reaction mixture, (b) weight fraction of the reaction mixture having a number-average degree of polymerization equal to 100,

Answer:

(a) for $x = 1$ and $p = 0.95$:

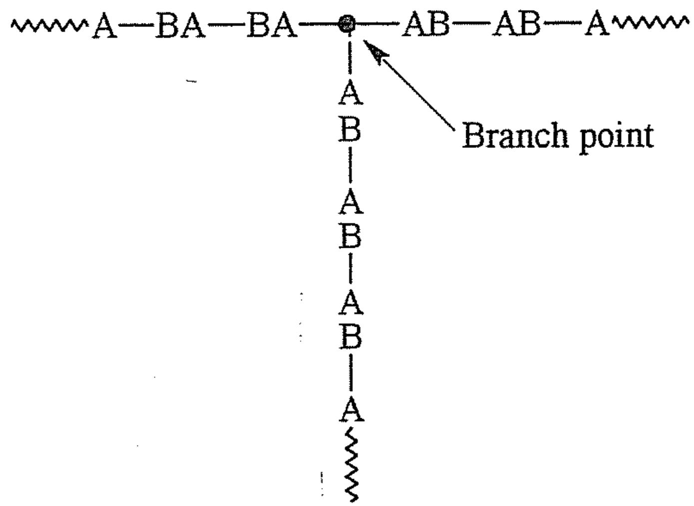
$$w_1 = (1)(1 - 0.95)^2(0.95)^0 = 2.5 \times 10^{-3} \quad \text{(i.e., } 0.25\% \text{ by weight)}$$

(b) for $x = 100$, $p = 0.95$:

$$w_{100} = (100)(1 - 0.95)^2(0.95)^{99} = 1.56 \times 10^{-3} \quad \text{(i.e., } 0.156\% \text{ by weight)}$$

Nonlinear Step Polymerization

Branching



A special kind of step-growth polymer may be produced by carrying out polymerization of an A—B type bifunctional monomer in the presence of a small amount of a second monomer A_f containing $f(>2)$ functional groups. The value of f represents the functionality of the monomer; thus, if $f = 3$, A_f represents a trifunctional monomer, $\bullet(-A)_3$, having three A end groups on the same molecule.

$$\overline{X}_n = (frp + 1 - rp)/(1 - rp)$$

$$\overline{X}_w = \frac{(f - 1)^2 (rp)^2 + (3f - 2)rp + 1}{(frp + 1 - rp)(1 - rp)}$$

$$\frac{\overline{X}_w}{\overline{X}_n} = 1 + \frac{frp}{(frp + 1 - rp)^2}$$

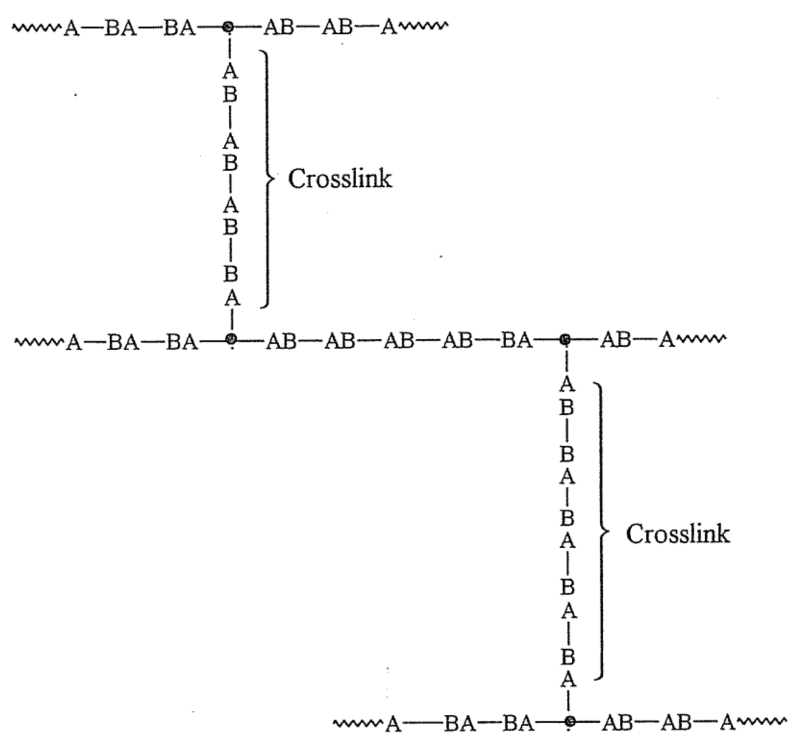
Crosslinking

Consider polymerization of a system consisting of

A—B, e.g., hydroxyacid HO–R–COOH

A_f ($f > 2$), e.g., triol $R'(OH)_3$

and B—B, e.g., dicarboxylic acid HOOC–R″–COOH



$$f_{av} = \frac{2N_{A_0}}{\sum N_{i_0}}$$

$$\overline{X}_n = \frac{2}{2 - p \cdot f_{av}}$$

$$p = \frac{2}{f_{av}} - \frac{2}{\overline{X}_n \cdot f_{av}}$$

$$\overline{X}_n \to \infty,$$

critical extent of reaction or *critical conversion*

$$p_c = \frac{2}{f_{av}}$$

Problem Can the following alkyd recipe be reacted to complete conversion of the limiting reactant without gelation ?

Phthalic anhydride $C_6H_4(CO)_2O$ = 2.0 mol
Glycerol $CH_2(OH)CH(OH)CH_2(OH)$ = 0.3 mol
Pentaerythritol $C(CH_2OH)_4$ = 0.6 mol

Answer:

Component	Moles	Functionality	Equivalents
Phthalic anhydride	2.0	2	4.0
Glycerol	0.3	3	0.9
Pentaerythritol	0.6	4	2.4
Total	2.9		7.3

Total acid equivalents = 4.0 and total OH equivalents = (0.9 + 2.4) = 3.3

since the OH equivalents are in deficient supply, $f_{av} = 2\times3.3/2.9 = 2.2759$. (Note that this represents the average **useful** functionality of the reaction mixture,

$$p_c = \frac{2}{f_{av}} = \frac{2}{2.2759} = 0.88$$