Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 3 - Molecular Weight Averages and Distributions

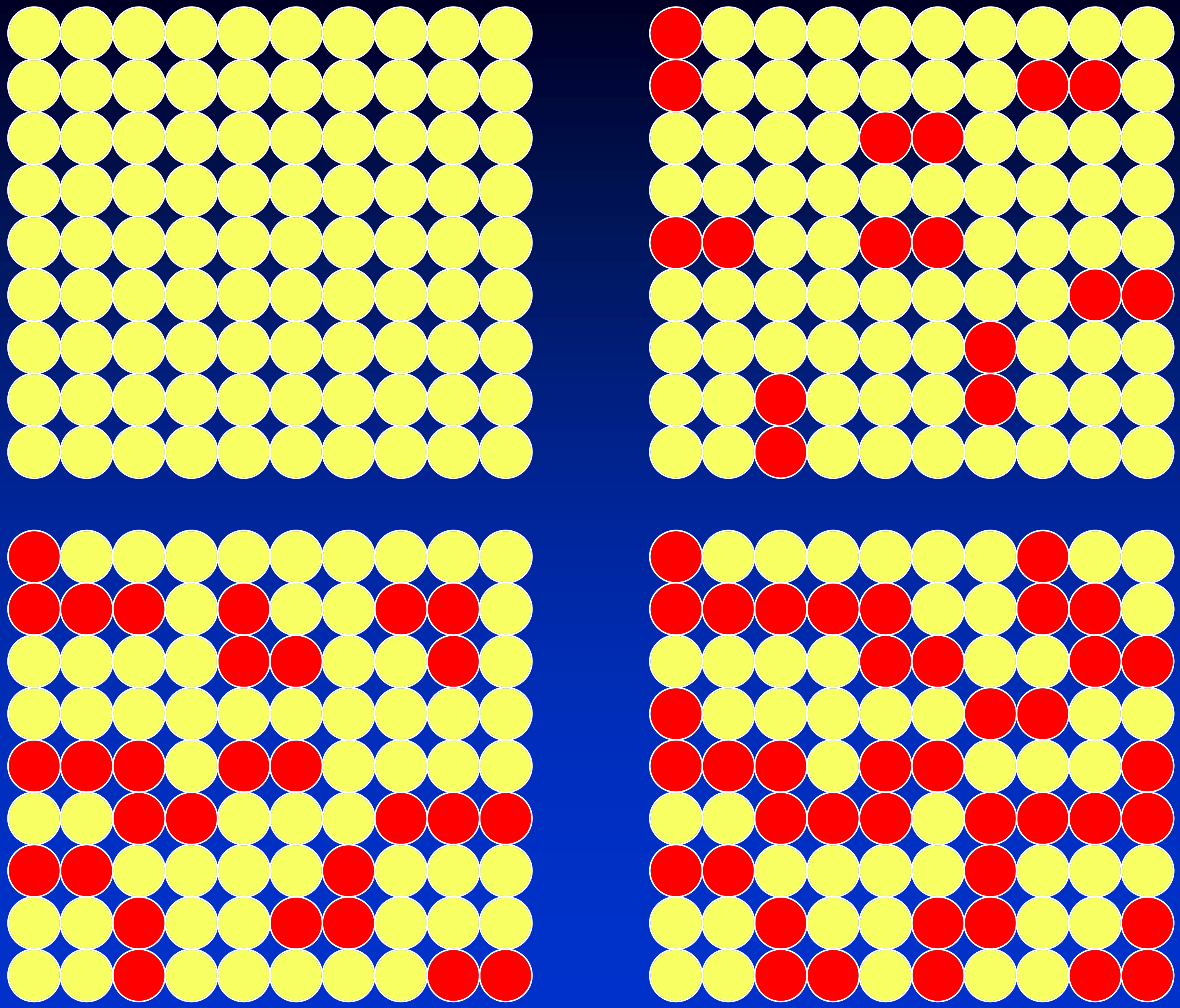
January 22, 2001

Reading: Sperling, Chapter 3

Outline

- Step-growth polymerization
- Number distribution and number average molecular weight (M_n)
- Weight distribution and weight average molecular weight (M_w)
- Breadth of distribution - polydispersity
- Integral expressions

Generic Scheme for A-B Reaction



Features of Step-Growth Polymerization

- Growth proceeds by a **step-wise** intermolecular reaction.
- Growth involves monomer units reacting with each other or with oligomers of **any size**.
- The reactivity of a functional group is **independent** of the size of the molecule to which it is attached.
- The reactivity of a functional group is **independent** of whether another functional group has previously reacted.
- High-molecular weight polymers are only produced after a **high degree of conversion** of functional groups.
- Step-growth polymerizations often involve an **equilibrium** between reactants and products, leading to **reversibility** and to **interchange** reactions.

Self Condensation of $HO(CH_2)_9COOH$

Mn	Number of ester groups	Spinnability
4,170	25	Absent
5,670	33	Short fibers, no cold drawing
7,330	43	Long fibers, no cold drawing
9,330	55	Long fibers that cold draw
16,900	99	Easy to spin and cold draw
25,200	148	Spins at T>210C and cold draws

Data from Organic Chemistry of Synthetic High Polymers, R. W. Lenz, 1967, p 66.

Arithmetic Mean

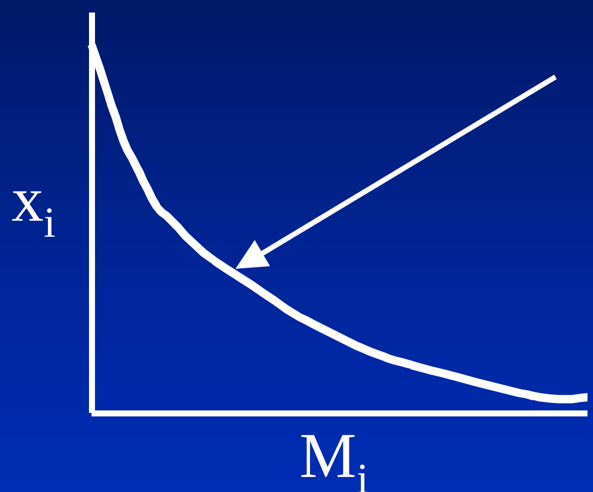
Our objective is to develop a parameter to express the **central tendency of the molecular weight distribution**. Assume a unit volume of a sample of N polymer molecules in which there are n_j molecules with molecular weight M_j. We determine the arithmetic mean molecular weight A as follows.

$$\sum_i n = N$$

$$A = \frac{\sum_i n_i M_i}{\sum_i n_i} = \frac{\sum_i n_i M_i}{N}$$

$$A = \sum_i \left(\frac{n_i}{N}\right) M_i = \sum_i f_i M_i$$

Differential Number Distribution



The area under the **differential** number distribution curve is unity if the distribution is normalized. Note that x_i is the **mole fraction**.

The **arithmetic mean** of the number distribution is given by

$$A = \sum x_i M_i = M_n \qquad (f_i \Rightarrow x_i)$$

This is referred to as the **number-average molecular weight.**

The number average molecular weight may be determined by colligative property measurements:

- Osmometry
- Vapor pressure change
- Freezing point depression (rare)
- Boiling point elevation (rare)

Most Probable Distribution for Linear Polymers

Consider the self-condensation of A-B and the stoichiometric polymerization of A-A with B-B where A may react only with B. This is equivalent to determining the probability of finding a polymer molecule containing x structural units of the form

$$\text{A-B [A-B]}_{x-2}\text{ A-B}$$

Let

p = probability that a B group has reacted. (This is equivalent to the fraction of B groups reacted.)

1 – p = probability that a B group is unreacted

In virtually all cases (except for polyurethanes) one can assume that the reaction events are independent. Thus, the probability that an x-mer has formed is given by

$$p^{x-1}(1-p)$$

Useful Infinite Summations

$$\sum_{1}^{\infty} p^x = \frac{p}{1-p}$$

$$\sum_{1}^{\infty} xp^{x-1} = \frac{\partial}{\partial p}\left[\sum_{1}^{\infty} p^x\right] = \frac{1}{(1-p)^2}$$

$$\sum_{1}^{\infty} (x+1)xp^{x-1} = \frac{\partial^2}{\partial p^2}\left[\sum_{1}^{\infty} p^{x+1}\right] = \frac{\partial^2}{\partial p^2}\left[p\sum_{1}^{\infty} p^x\right]$$

$$= \frac{2}{(1-p)^3}$$

$$\sum_{1}^{\infty} x^2 p^{x-1} = \sum_{1}^{\infty} (x+1)xp^{x-1} - \sum_{1}^{\infty} xp^{x-1} = \frac{1+p}{(1-p)^3}$$

Number Fraction Distribution

Let

N(x) = number of x-mers

N = total number of polymer molecules

Then the number fraction, N_x , is given by

$$N_x = N(x)/N$$

But this is just the probability that an x-mer has formed. Thus, the <u>number fraction distribution</u> function is given by

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

Most Probable Distribution: Number Fraction

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

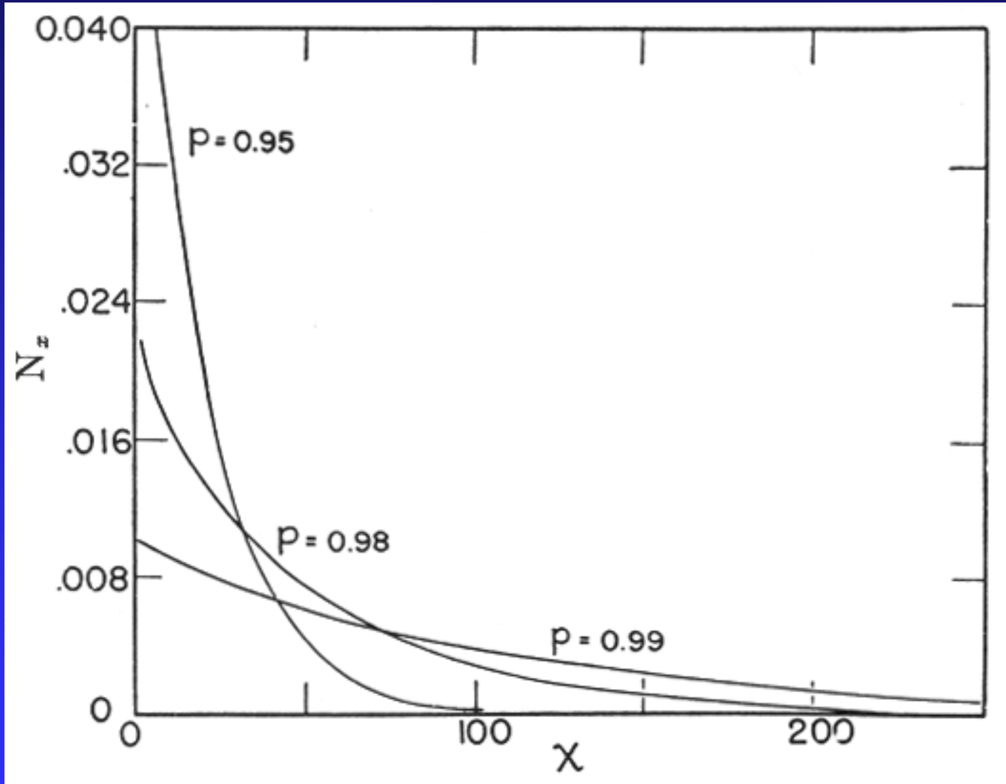


FIG. 51.—Mole fraction distribution[1] of chain molecules in a linear condensation polymer for several extents of reaction p.

P.J. Flory, Principles of Polymer Chemistry, 1953, p 321.

Number Average Molecular Weight

The **number average molecular weight** is defined by

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

Dividing by the repeat unit weight M_o yields

$$x_n = \frac{M_n}{M_o} = \frac{\sum_i N_x \left(\frac{M_x}{M_o}\right)}{\sum_i N_x} = \frac{\sum_x xN_x}{\sum_x N_x} = \sum_x xN_x$$

Substitution of the **"most probable"** number distribution gives

$$x_n = \sum_x xp^{x-1}(1-p) = \frac{1-p}{(1-p)^2} = \frac{1}{1-p}$$

This is the **number average degree of polymerization.**

Carothers Equation

This provides an alternative approach to X_n that is based completely on **stoichiometric** considerations. Its main purpose is to provide a basis for more complex systems.

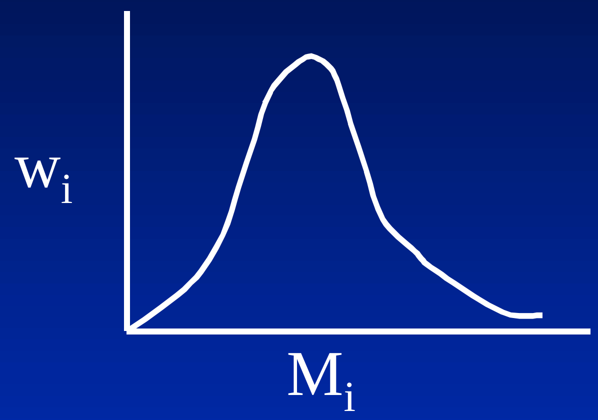
p = **extent of reaction** (probability that any functional group present in the initial reaction mixture has reacted)

$$p = \frac{N_o - N}{N_o}$$

$$\frac{N_o}{N} = \frac{1}{1-p} = \overline{X}_n$$

p	0.5	0.90	0.99	0.999	0.9999
X_n	2	10	100	1000	10,000

Differential Weight Distribution



The area under this **differential** weight distribution curve is unity if the distribution is normalized.

If we select the **weight fraction** as the weighting function, that is if we let $f_i \Rightarrow w_i$, we obtain the **weight average molecular weight** $\mathbf{M_w}$**.**

$$A = \sum_i w_i M_i = M_w$$

The weight average molecular weight may be determined experimentally by

- Scattering measurements
  - Light
  - X-rays
  - Neutrons
- Sedimentation equilibrium (ultracentrifuge)

Weight Fraction Distribution

Begin with the number fraction distribution to obtain

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

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

If N_o = number of structural units present initially,

$N = N_o(1 - p)$

$N(x) = N_o(1 - p)^2\, p^{x-1}$

We define the weight fraction by

$W_x = xN(x) / N_o$

Thus, the <u>weight fraction distribution</u> is given by

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

Most Probable Distribution: Weight Fraction

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

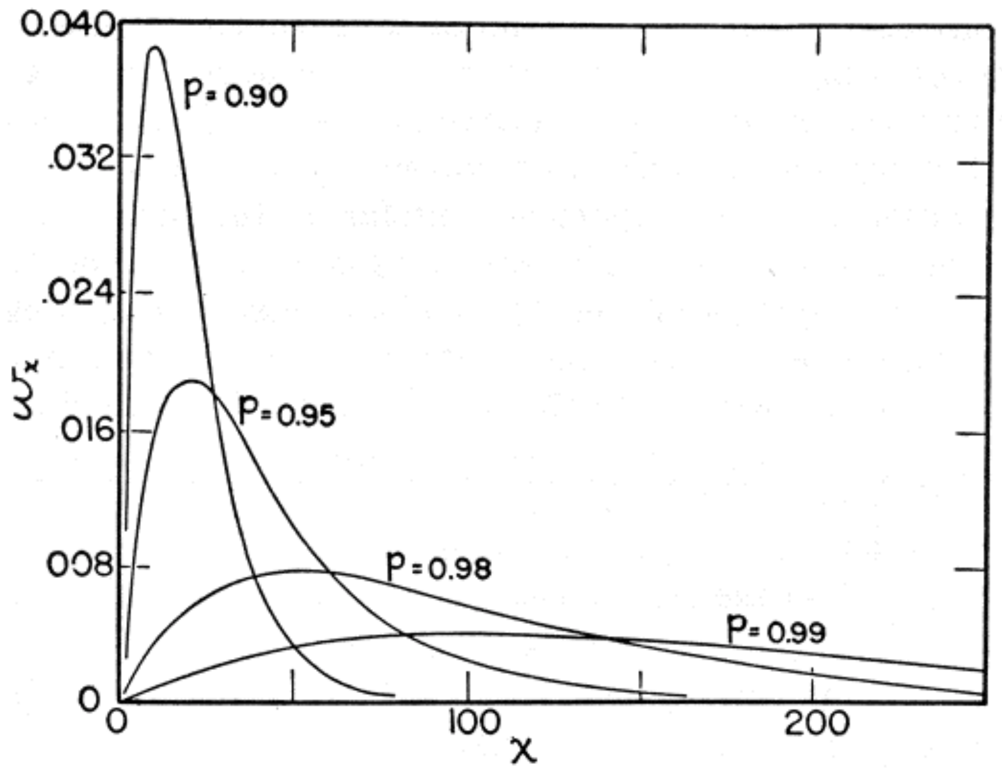


FIG. 52.—Weight fraction distributions[1] of chain molecules in linear condensation polymers for several extents of reaction *p*.

P.J. Flory, <u>Principles of Polymer Chemistry</u>, 1953, p 322.

Weight Average Degree of Polymerization

By analogy to the number average, we may write

$$x_w = \sum_x xW_x$$

Substitution of the **"most probable"** weight distribution gives

$$x_w = \sum_x x^2 p^{x-1}(1-p)^2 = \frac{(1+p)(1-p)^2}{(1-p)^3} = \frac{1+p}{1-p}$$

Polydispersity

A convenient parameter that characterizes the breadth of the molecular weight distribution is the **polydispersity**.

$$\frac{x_w}{x_n} = \frac{M_w}{M_n} = 1 + p$$

Note that as the polymerization reaction goes to completion, p approaches unity and

$$\frac{M_w}{M_n} \rightarrow 2$$

Equivalent Definitions of M_n and M_w

Number average molecular weight

$$M_n = \frac{\sum_i c_i}{\sum_i \frac{c_i}{M_i}} = \frac{1}{\sum_i \frac{w_i}{M_i}}$$

Weight average molecular weight

$$M_w = \frac{\sum_i c_i M_i}{\sum_i c_i} = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

Breadth of the Distribution

Standard deviation of the number distribution

$$s_n = \left(M_w M_n - M_n^{\,2}\right)^{0.5}$$

$$\frac{s_n^{\,2}}{M_n^{\,2}} = \frac{M_w}{M_n} - 1$$

Standard deviation of the weight distribution

$$\frac{s_w^{\,2}}{M_w^{\,2}} = \frac{M_z}{M_w} - 1$$

Note: M_n and M_w are easy to obtain experimentally, but M_z is difficult to obtain (must use ultracentrifuge).

Integral Expressions

Molecular weight distributions can be regarded as **continuous** so that integral expressions are valid.

The proportion of a sample with molecular weight between M and M + dM is f(M)dM, where
f(M) = x(M) for a number distribution and
f(M) = w(M) for a weight distribution.

$$A = \int_0^\infty f(M) M dM$$

Average Molecular Weights from Integral Expressions

$$M_n = \int_0^\infty Mx(M)dM = \frac{1}{\int_0^\infty \frac{w(M)dM}{M}}$$

$$M_w = \int_0^\infty Mw(M)dM$$

$$M_z = \frac{\int_0^\infty M^2 w(M)dM}{\int Mw(M)dM}$$