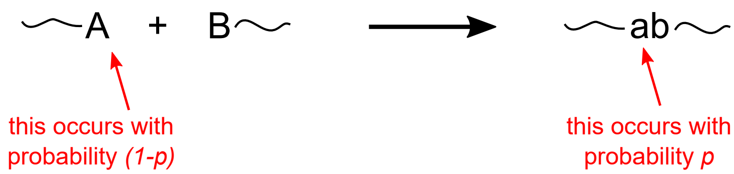
Molecular Weight Distributions in Step-Growth Polymerizations

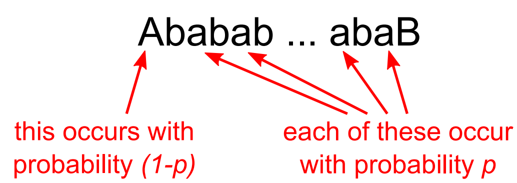
Model 1: Probabilities of Forming Different Chain Lengths

Recall that in a step-growth polymerization of AB-type monomers, the extent of reaction p gives the fraction of 'A' groups that have reacted.

In terms of probabilities, the *probability* that a particular 'A' group reacts (turns into an 'a' group) is p, while the probability that it *does not* react (remains an 'A' group) is $1-p$:



Each molecule has some combination of unreacted 'A' groups and reacted 'a' groups, each of which occurs with probability p or $(1-p)$ as appropriate:



The *total* probability of forming this molecule is just the product of the probabilities for each group:

$$P(molecule) = \underbrace{(p \times p \times p \times \ldots)}_{\text{one factor of p for each reacted 'a' group}} \times \underbrace{((1-p) \times (1-p) \times \ldots)}_{\text{one factor of (1-p) for each unreacted 'A' group}}$$

or, more concisely,

$$P(molecule) = p^{(\text{number of reacted 'a' groups})} \times (1-p)^{(\text{number of unreacted 'A' groups})}$$

Critical Thinking Questions:

1. Consider an AbabaB trimer:

   a) How many monomers came together to form this molecule (that is, what is its degree of polymerization)?

   b) How many *unreacted* 'A' groups are in this molecule?

c) How many *reacted* ‘a’ groups are in this molecule?

d) What is the probability of forming an AbabaB trimer?

2. More generally, consider a molecule with degree of polymerization i (that is, a molecule that was made by linking together i AB-type monomers).

   a) How many *unreacted* ‘A’ groups are in this molecule?

   b) How many *reacted* ‘a’ groups are in this molecule?

   c) What is the probability of forming a molecule with degree of polymerization i?

Information:

The *probability* that a molecule is has degree of polymerization i is the same as the *fraction of molecules* that have degree of polymerization i.

Critical Thinking Questions:

3. Complete the following statement:

   “The fraction of molecules, x_i, that have degree of polymerization i is __________.”

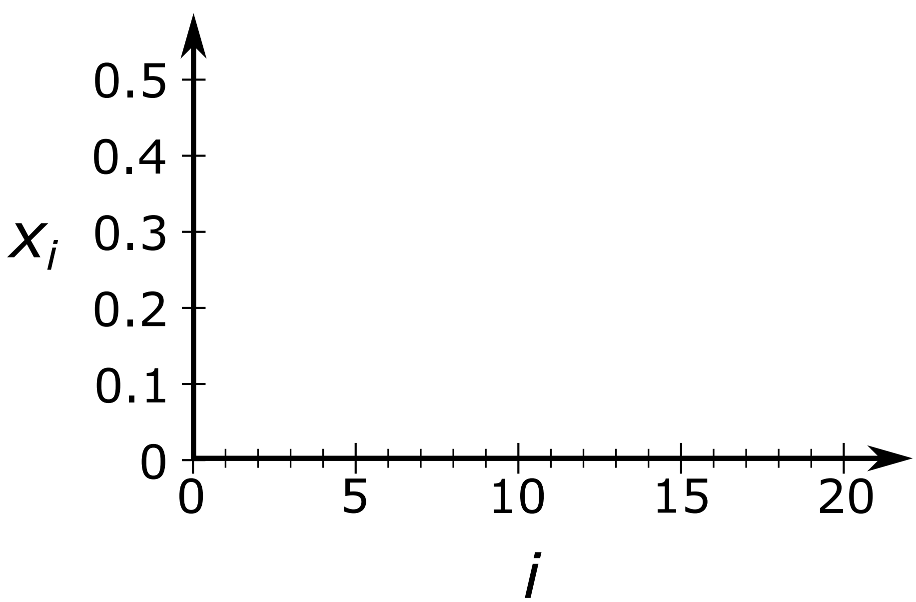
Model 2: Chain Length Distributions

The following table gives selected values of x_i calculated at two different extents of reaction, p, using the expression you derived in Model 1:

i	x_i when $p = 0.5$	x_i when $p = 0.9$
1	0.5	0.1
2	0.25	0.09
3	0.125	0.08
5	0.0313	0.065
10	9.7x10^{-4}	0.0387
15	3.1x10^{-5}	0.0229
20	9.5x10^{-7}	0.0135

Critical Thinking Questions:

4. Plot the data given in Model 2 on the following axes. Make sure to use a different symbol for points corresponding to $p = 0.5$ than for the points corresponding to $p = 0.9$.



5. How are the plots for $p = 0.5$ and $p = 0.9$ similar, and how are they different? Briefly describe your observations in 2-3 complete sentences.

6. What is the *most probable* chain length for each value of p? Briefly explain your answer in 1-2 complete sentences.

7. Can the fraction of chains with length $i + 1$ ever be *greater* than the fraction of chains with length i? Justify your answer in 2-3 complete sentences.

Model 3: M_n and M_w for Step-Growth Polymerizations

To calculate M_n and M_w, we need to know n_i, or the total number of chains with i monomers.

If we started with v_A^0 monomers, then when the extent of reaction is equal to p, there will be $(1-p)v_A^0$ unreacted A groups left. Recalling that the number of unreacted A groups is equal to the number of molecules in the reaction mixture, this lets us write

$$\begin{aligned} n_i &= \text{(fraction of molecules that have length } i\text{) x (number of molecules in reaction mixture)} \\ &= \left(p^{i-1}(1-p)\right)\left((1-p)v_A^0\right) \\ &= p^{i-1}(1-p)^2 v_A^0 \end{aligned}$$

If we plug this expression into our equation for M_n, we get

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} = M_0 \frac{\sum_i p^{i-1}(1-p)^2 i}{\sum_i p^{i-1}(1-p)^2}$$

where M_0 is the molecular weight of the monomer ($M_i = M_0 i$).

Evaluating these sums (see Exercise 2), we obtain

$$M_n = \frac{M_0}{1-p} \qquad \text{or} \qquad N_n = \frac{M_n}{M_0} = \frac{1}{1-p}$$

which is exactly what we came up with in our previous activity on degree of polymerization.

Similarly, plugging the above expression for n_i into our expression for M_w and evaluating the sums, we obtain

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} = M_0 \frac{1+p}{1-p} \qquad \text{or} \qquad N_w = \frac{M_w}{M_0} = \frac{1+p}{1-p}$$

Critical Thinking Questions:

8. Calculate the dispersity for a step-growth reaction with extent of reaction p.

9. What is the value of the dispersity when $p = 0$? Briefly comment on whether or not this answer makes sense.

10. What is the value of the dispersity when $p = 1$?

11. Can the dispersity of a polymer produced by a step-growth polymerization ever be greater than 2? Briefly defend your answer in 1-2 complete sentences.

Exercises:

1. Suppose you synthesized a polymer by step-growth polymerization and found that it had a dispersity of 1.86.

   a) What must the extent of reaction have been in this polymerization?

   b) What would you expect the number-average degree of polymerization of this polymer to be?

2. Show that the summation expression for M_n given in Model 3 simplifies to the expected result by doing the following:

   a) First, show that the summation expression for M_n given in Model 3 can be rewritten

$$M_n = M_0 \frac{\sum_i ip^{i-1}}{\frac{1}{p}\sum_i p^i}$$

b) The denominator of this expression is just a geometric series. Recall that if $p < 1$, then

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

Substitute this expression into your equation for M_n and simplify.

c) The remaining sum can be calculated by differentiating both sides of the equation for $\sum_i p^i$. Carry out this differentiation to show that

$$\sum_{i=1}^{\infty} i p^{i-1} = \frac{1}{(1-p)^2}$$

d) Finally, substitute this expression into M_n and show that you obtain the expected solution.