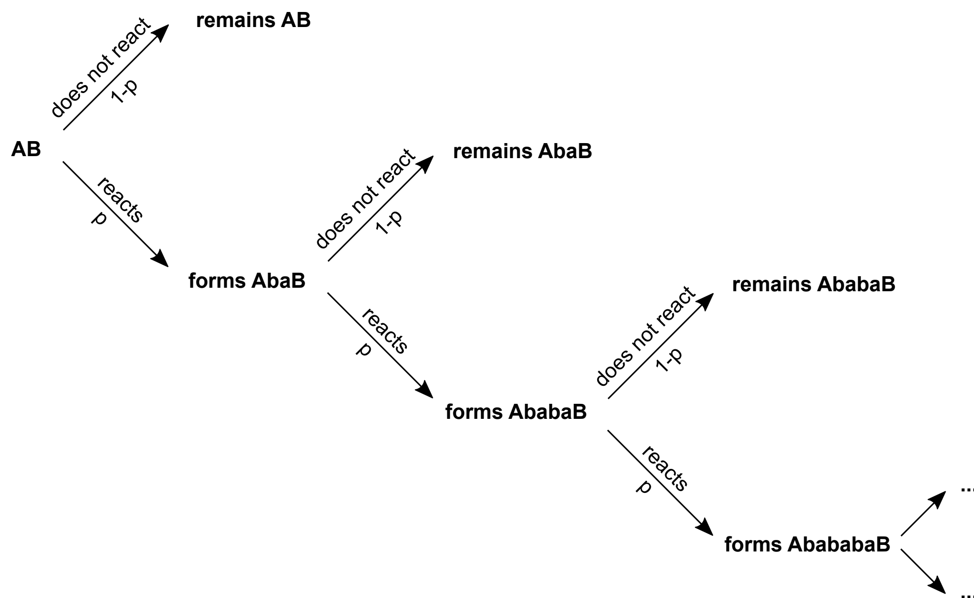
Molecular Weight Distributions in Step-Growth Polymerizations

Model 1: Probabilities of Forming Different Chain Lengths

To determine the *distribution* of chain lengths formed in a step-growth polymerization, it is useful to calculate the probability of forming each different chain length.

The following diagram summarizes the steps that lead to different chain lengths in a step-growth polymerization of AB-type monomers at extent of reaction p:



In this diagram, the different **states** of the polymer chain are written in bold text. They are connected by arrows describing the **processes** that take the chain from one state to the next; the text *above* each arrow describes which process takes place, while the expression *under* each arrow gives the probability of that process occurring.

Critical Thinking Questions:

1. What is the probability that...

   a) ... an AB monomer does not react, and remains an AB monomer?

   b) ... an AB monomer reacts to form an AbaB dimer?

   c) ... an AbaB dimer does not react, and remains an AbaB dimer?

d) ... an AbaB dimer reacts to form an AbabaB trimer?

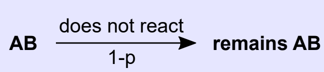
2. For *any* molecule with n monomers, what is the probability that it reacts to form a molecule with $n+1$ monomers?

3. Is your answer to the previous question consistent with the definition of the extent of reaction p? Briefly explain your answer in 1-2 complete sentences.

Information:

For a process with a **single** step, the overall probability of reaching the final state is just the probability of that step.

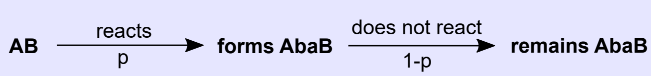
For example, the series of steps that leads to a chain with exactly one monomer (i.e. an AB monomer that does not react) is shown below:



Since there is only a single step in this process, the overall probability of obtaining a chain with exactly 1 monomer is just the probability of this step, or $1-p$.

For processes with **multiple** steps, the overall probability of reaching the final state is the *product* of the probabilities for each step in the process.

For example, the series of steps takes us from an initial AB monomer to an AbaB chain that does not react further (remains a chain with exactly 2 monomers) is:



The first step occurs with probability p, while the second step occurs with probability $1-p$; the total probability of obtaining a chain with exactly 2 monomers is the product of these probabilities, or $p(1-p)$.

Critical Thinking Questions:

4. Diagram the series of steps that lead to formation of a chain with 3 monomers that does not react any further:

5. Based on your diagram, what is the overall probability of obtaining a chain with exactly 3 monomers?

6. Building on this process, fill in the blanks in the following table:

i	**Probability that a molecule is composed of exactly i monomers**
1	$1 - p$
2	$p(1 - p)$
3	
4	
5	

7. What pattern do you notice in these values? Briefly describe your observations in 1-2 complete sentences.

8. Complete the following statement:
   "The probability that a molecule is composed of exactly i monomers is ________."

Information:

The *probability* that a molecule is composed of exactly i monomers is the same as the *fraction of molecules* that are composed of exactly i monomers.

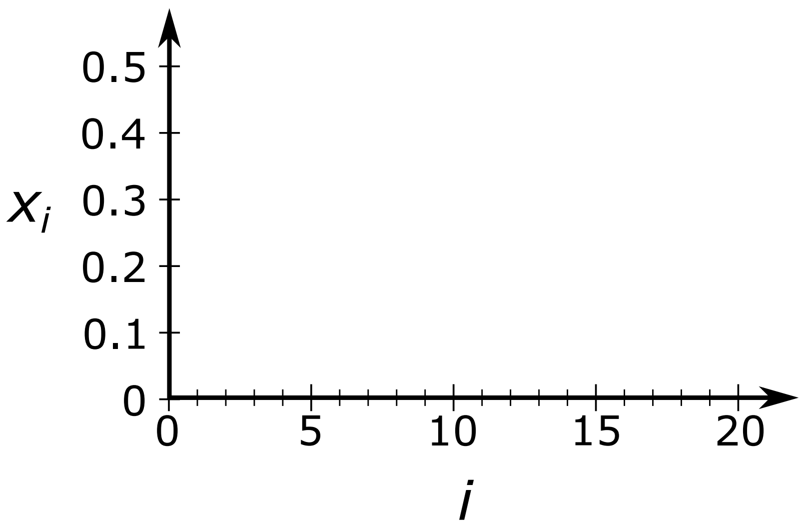
Critical Thinking Questions:

9. Complete the following statement:
   "The fraction of molecules, x_i, that are composed of exactly i monomers is ________."

10. Using this expression, calculate the fraction of molecules that have exactly length i for both $p = 0.5$ and $p = 0.9$ at the following values of i:

i	x_i when $p = 0.5$	x_i when $p = 0.9$
1		
2		
3		
5		
10		
15		
20		

11. Plot your results on the following axes. Make sure to use a different symbol for points corresponding to $p = 0.5$ than for the points corresponding to $p = 0.9$.



12. 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.

13. What is the *most probable* chain length for each value of p?

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

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Model 2: 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

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

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 ($M_i = M_0 i$).

If we evaluate these sums, 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 expected (whew - our math worked!).

Similarly, if we plug this expression into our equation for M_w and work through the sums, we get

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

Critical Thinking Questions:

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

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

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

18. Can the dispersity of a polymer produced by 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 2 simplifies to the expected result by doing the following:
   a) First, show that the summation expression for M_n given in Model 2 can be rewritten

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

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.