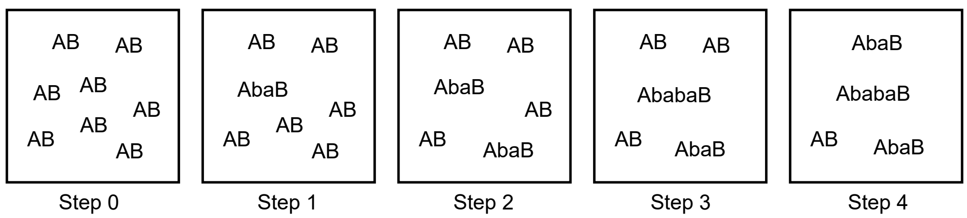
Degree of Polymerization in Step-Growth Polymerizations

Model 1: Polymerization of “AB”-Type Monomers

The simplest type of step-growth polymerization is one in which each monomer has one “A”-type reactive group and one “B”-type reactive group. These types of monomers are referred to as “AB”-type monomers.

In each step of the polymerization, an “A” group on one molecule reacts with a “B” group on another molecule to form an “ab” bond, as shown below:

For example, for a simple reaction mixture containing 8 “AB”-type monomers, the evolution of the reaction mixture might look something like this:



Critical Thinking Questions:

1. For the reaction mixture shown in Model 1, fill out the following table. When counting the number of molecules, make sure to count *both* the unreacted monomers and the growing oligomer/polymer chains (that is, you should count each ‘AB’, ‘AbaB’, ‘AbabaB’, etc. as one molecule).

Step	**Number of unreacted “A” groups**	**Number of molecules**
0		
1		
2		
3		
4		

2. Explain, in a complete sentence, how the number of molecules in the mixture is related to the number of unreacted "A" groups.

Information:

At any given time, the number-average degree of polymerization, N_n, is the total *initial* number of monomers divided by the total number of molecules *currently* present. That is,

$$N_n = \frac{\text{initial number of monomers}}{\text{current number of molecules}}$$

Critical Thinking Questions:

3. In Model 1, there were 8 monomers in the initial reaction mixture. Using this information, calculate the number-average degree of polymerization for each step shown in Model 1.

Step	**0**	**1**	**2**	**3**	**4**
$\mathbf{N_n}$					

4. Suppose that you had initially started with 100 monomers. Then, suppose that at some time later, you had only 8 unreacted "A" groups left.

   a) How many molecules would there be in the reaction mixture at this point?

   b) What would the number-average degree of polymerization be at this point?

5. More generally, suppose you started with v_A^0 monomers, and at some time later, you had only v_A unreacted "A" groups left. What would the number average-degree of polymerization be at this point, in terms of v_A^0 and v_A?

Information:

Usually, we find it more useful to work in terms of the *fraction* of all "A" groups that have reacted, rather than the total *number* of "A" groups that have reacted.

In step-growth polymerizations, we refer to the fraction of "A" groups that have *reacted* as the "extent of reaction", p. When the fraction of "A" groups that *have* reacted is p, the fraction of "A" groups that have *not* reacted is $1 - p$.

Critical Thinking Questions:

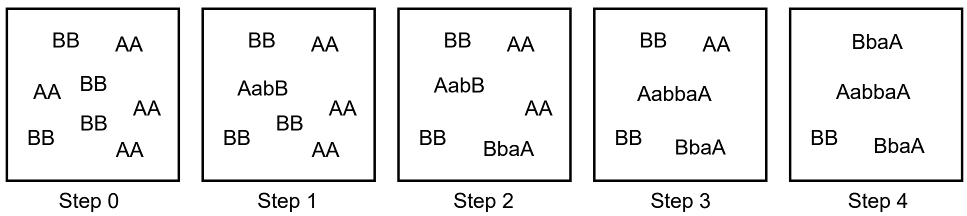
6. If we start with v_A^0 "A" groups, what is v_A (that is, how many "A" groups are still unreacted) when the extent of reaction is equal to p?

7. Using your answers to critical thinking questions 5 and 6, derive an expression for N_n in terms of p.

Model 2: Polymerization of "AA" and "BB"-Type Monomers

Now, let's consider a slightly more complicated reaction, with two different types of monomers that each have *either* two "A" reactive groups *or* two "B" type reactive groups. We call monomers with two "A" groups "AA"-type monomers, and we call monomers with two "B" groups "BB"-type monomers.

Suppose we start with 4 "AA"-type monomers and 4 "BB"-type monomers. In this case, the evolution of the reaction mixture might look something like this:



Critical Thinking Questions:

8. For the reaction mixture shown in Model 2, fill out the following table:

Step	Number of unreacted "A" groups	Number of molecules	N_n
0			
1			
2			
3			
4			

9. Compare your answers in question 8 with those from question 1. What similarities and/or differences do you notice?

10. Consider the following statement:

    "In polymerizations of AA- and BB-type monomers, we should be able to use the same expressions to calculate N_n as we did for polymerizations of AB-type monomers."

    In two or three complete sentences, briefly critique or defend this statement, making sure to explain your reasoning.

Information:

> A reaction is *stoichiometrically balanced* if the initial reaction mixture contains exactly the same number of "A" and "B" reactive groups.

Critical Thinking Questions:

11. Are the reactions in Models 1 and 2 stoichiometrically balanced? Briefly explain your answer in one or two complete sentences.

12. Predict what the reaction mixtures in Models 1 and 2 might look like if you let them react until no more reactions could take place:

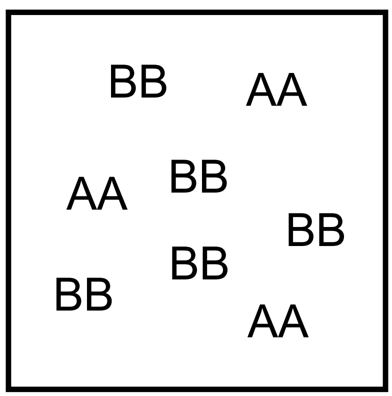
Model 1 Model 2

13. Calculate the number-average degree of polymerization for both of the "final" states you drew in response to the previous question:

Model 3: A Stoichiometrically-Imbalanced Reaction Mixture

Practically speaking, it is often very difficult to ensure that a reaction mixture is perfectly stoichiometrically-balanced, and there is often a small excess of one type of monomer or the other.

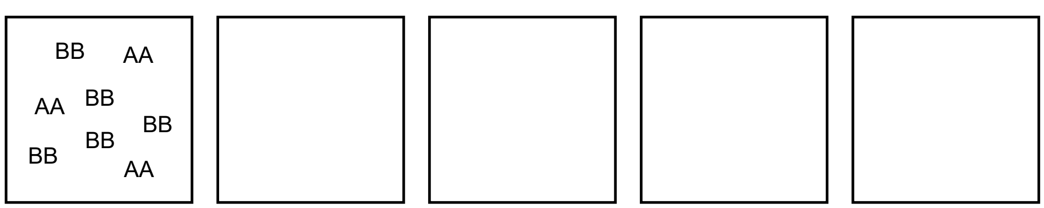
In this model, consider a reaction mixture that starts with 3 AA-type monomers and 5 BB-type monomers:



Step 0

Critical Thinking Questions:

14. Fill in the blank spaces in the figure below with reasonable predictions for what the reaction mixture might look like in each successive step.



Step 0 Step 1 Step 2 Step 3 Step 4

15. Which type of reactive group is the "limiting reagent" in this reaction? Briefly explain your reasoning.

16. Predict what the reaction mixture in Model 3 might look like if you let it react until no more reactions could take place:

Model 3

17. Calculate the number-average degree of polymerization for the "final" state you drew in response to the previous question:

18. Is the final degree of polymerization for this stoichiometrically-unbalanced reaction smaller than, equal to, or larger than the final degree of polymerization you calculated for the stoichiometrically-balanced reactions in Models 1 and 2?

19. Which type of reactive group is on the ends of all of the chains you drew in question 16?

20. Briefly critique or defend the following statement:

    "When drawing the structure of a polymer produced by a step-growth polymerization, we should always make sure that we draw end groups consistent with whichever reactive species was present in excess."

Information:

In stoichiometrically-imbalanced step-growth polymerizations with an excess of B groups, we define a parameter r that reflects the ratio of A groups to B groups. If the initial number of A groups is v_A^0 and the initial number of B groups is v_b^0, then

$$r = \frac{v_A^0}{v_B^0}$$

For a reaction mixture with stoichiometric imbalance r at extent of reaction p, the number-average degree of polymerization is given by

$$N_n = \frac{1+r}{1+r-2pr}$$

Critical Thinking Questions:

21. Using this expression, fill in the following table with the expected number-average degree of polymerization for different combinations of r and p values:

	$p = 0.9$	$p = 0.99$	$p = 0.999$
$r = 0.9$			
$r = 0.99$			
$r = 0.999$			

22. On the basis of your answers to the previous question, briefly critique or defend the following statement:

    "Achieving high molecular weights in step-growth polymerizations requires both very precise measurement of the reagents, and reaction conditions which strongly favor the bond-forming reaction."

Exercises:

1. In the stoichiometrically-balanced reactions in models 1 and 2, the number of molecules was equal to the number of unreacted 'A' groups in each step. Is the same thing true for the stoichiometrically-imbalanced reaction in Model 3? Why or why not?

2. In this activity, we only calculated the number-average *degree of polymerization* of the polymers produced in step-growth polymerizations. However, usually, we want to be able to calculate the *molecular weight* of the polymers as well.

   a) In Model 1, we considered a reaction of AB-type monomers. If each monomer had mass m_{AB}, how would you calculate the number-average molecular weight, M_n, of the polymer produced when the extent of reaction is equal to p?

   b) In Model 2, we considered a stoichiometrically-balanced reaction of AA- and BB-type monomers. If the AA-type monomers each had mass m_{AA} and the BB-type monomers each had mass m_{BB}, how would you calculate the number-average molecular weight of the polymer produced when the extent of reaction is equal to p?

      Note: this question is a little tricky - remember that N_n counts monomers, *but in this reaction, not all of the monomers have the same molecular weight. How might you be able to correct for this?*

3. In Model 3, we considered a stoichiometrically-imbalanced reaction of AA- and BB-type monomers. However, another important limit occurs when we have equal numbers of AA- and BB-type monomers, but add in an extra monofunctional reagent "Bx" that can only react on one side.

   In this exercise, suppose that we have v_A^0 'A' groups from AA-type monomers, v_B^0 'B' groups from BB-type monomers, and $v_{B'}^0$ 'B' groups from Bx-type molecules.

   a) Consider the following statements from two students:

      - **Student 1:** *"The total number of 'B' groups is just $v_B^0 + v_{B'}^0$, so we can account for the presence of monofunctional Bx molecules by replacing $r = \frac{v_A^0}{v_B^0}$ with $r' = \frac{v_A^0}{v_B^0 + v_{B'}^0}$."*

- **Student 2:** *"One Bx molecule has the same effect on the degree of polymerization as one BB-type molecule. Since Bx-type molecules have the same effect with half as many 'B' groups, that means that a 'B' group from a Bx molecule is twice as effective at stopping chain growth as a 'B' group from a BB molecule, so we should replace r with* $r' = \frac{v_A^0}{v_B^0 + 2v_{B'}^0}$*."*

Which student do you agree with, and why?

b) Monofunctional reagents are a common impurity in supplies of difunctional monomers. Briefly explain why this means it is necessary to rigorously purify the starting materials used in step-growth polymerizations.

