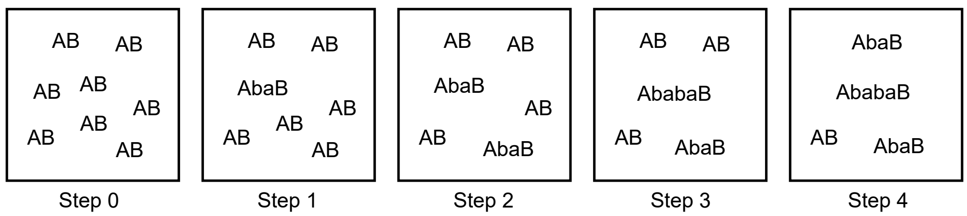
Degree of Polymerization in Step-Growth Polymerizations

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:



In this diagram, each string of letters represents one molecule; each molecule may be either an unreacted monomer ("AB") or a growing polymer chain (e.g. "AbaB", "AbabaB", etc.).

Critical Thinking Questions:

1. Fill out the following table for the reaction mixture shown in Model 1:

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

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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:

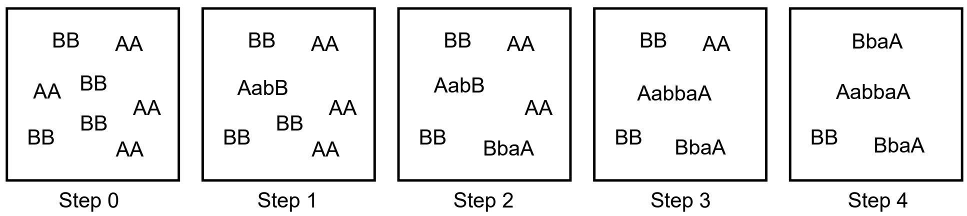
6. If we start with v_A^0 "A" groups, what is v_A (that is, how many "A" groups are still unreacted) when the extent of reaction is equal to p?

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 8 monomers, 4 of which are "AA"-type monomers and 4 of which are "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**	$\mathbf{N_n}$
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

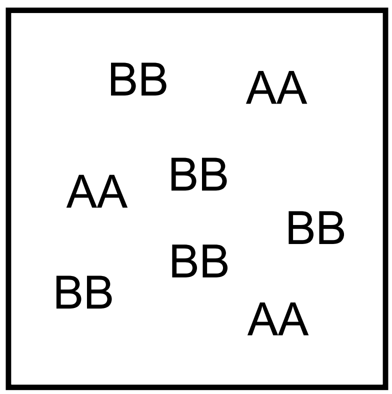
Model 2

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 perfecty stoichiometrically-balanced, and there is often a small excess of one type of monomer or the other.

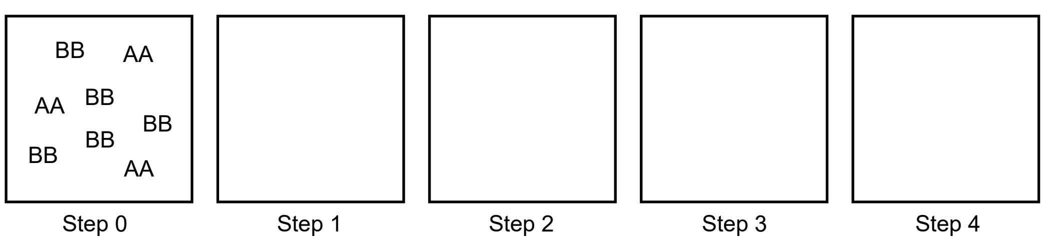
In this model, consider a reaction mixture that starts with 3 AA-type monomers and 5 BB-type monomers:



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.



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. Often, when calculating extents of reaction and degrees of polymerization, our usual rules regarding significant figures don't work well. To see why, do the following:

   a) Rearranging our equation for N_n for a stoichiometrically-balanced reaction and solving for p, we find that $p = \frac{N_n - 1}{N_n} = 1 - \frac{1}{N_n}$.
   Using this equation, calculate the extent of reaction necessary to reach each of the following degrees of polymerization. Write out as many digits as your calculator gives you.

N_n	p
10	
100	
300	
320	
1000	
10000	

b) How many significant figures are given in each of the N_n values in the preceding problem? What value(s) would you get for p if you round your answer following the usual sig fig rules?

c) In the context of your results, does the "usual" rule for sig figs make sense when calculating extents of reactions? Explain your reasoning in 1-2 complete sentences.

d) Propose an alternate sig fig rule that would make more sense for calculating extents of reaction.

2. 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?

3. 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?*

4. 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.