

Degree of Polymerization in Step-Growth Polymerizations

Instructor Notes:

This activity introduces students to key concepts related to the degree of polymerization and stoichiometric balance in step-growth polymerizations.

After completing this activity, students will be able to:

1. Calculate the number-average degree of polymerization for stoichiometrically-balanced step-growth polymerizations of 'AB' or 'AA+BB' monomer mixtures
2. Explain what it means for a reaction to be stoichiometrically-balanced
3. Describe the consequences of stoichiometric imbalance in terms of (a) the degree of polymerization and (b) the end-group functionality of the polymer chains.

This activity will prepare students for follow-up activities on the chemistry, equilibria, kinetics, and molecular-weight distributions of step-growth polymerizations.

Activity summary:

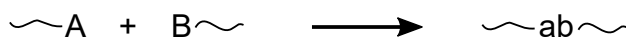
- **Activity type:** Learning Cycle
- **Content goals:** Stoichiometry and degree of polymerization in step-growth polymerizations
- **Process goals:** written communication, critical thinking, information processing
- **Duration:** approx. 45 minutes without class discussion
- **Instructor preparation required:** none beyond knowledge of relevant content
- **Related textbook chapters:**
 - *Polymer Chemistry* (Hiemenz & Lodge): sections 2.2 and 2.7

Degree of Polymerization in Step-Growth Polymerizations

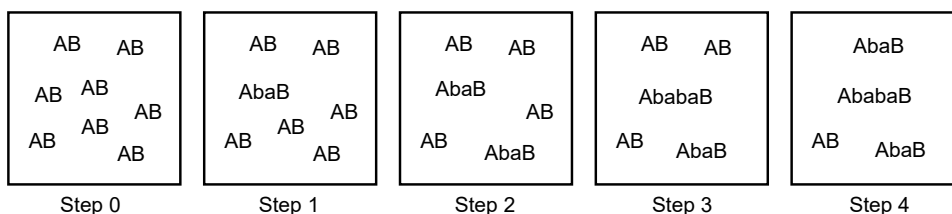
Model 1: Polymerization of “AB”-Type Monomers

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:

- 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	8	8
1	7	7
2	6	6
3	5	5
4	4	4

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

The number of molecules in the mixture is exactly equal to the number of unreacted ‘A’ groups at each step of the reaction.

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
N_n	8	$8/7=1.14$	$8/6=1.33$	$8/5=1.6$	$8/4=2$

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?

8

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

$100/8 = 12.5$

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 ?

$$N_n = \frac{v_A^0}{v_A}$$

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 ?

$$v_A = (1 - p)v_A^0$$

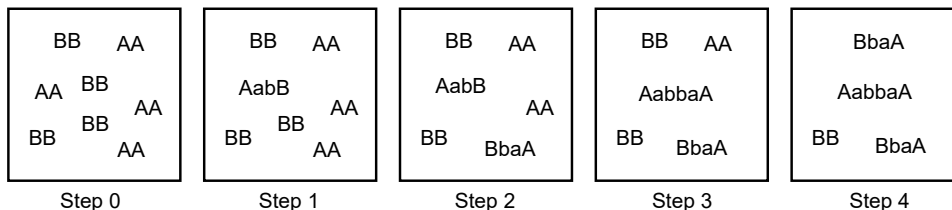
7. Using your answers to critical thinking questions 5 and 6, derive an expression for N_n in terms of p .

$$N_n = \frac{v_A^0}{v_A} = \frac{v_A^0}{(1-p)v_A^0} = \frac{1}{1-p}$$

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	8	8	$8/8=1$
1	7	7	$8/7=1.14$
2	6	6	$8/6=1.33$
3	5	5	$8/5=1.6$
4	4	4	$8/4=2$

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

The numbers are exactly the same - the ‘AA+BB’ reaction behaves exactly the same as the polymerization of ‘AB’ monomers.

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.

DEFEND: In both types of polymerizations, one step of the reaction uses up one ‘A’ reactive group and decreases the total number of molecules by one. Thus, in both types of reactions, the total number of molecules will always be equal to the number of unreacted ‘A’ groups, so at the same extent of reaction p we should have the same number of molecules and thus the same molecular weight regardless of the type of monomers we started with.

Information:

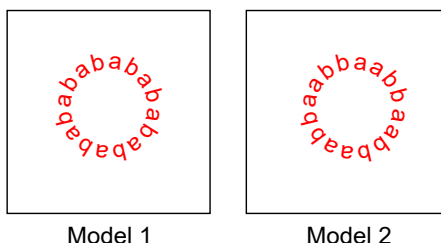
A reaction is *stoichiometrically balanced* if the initial reaction mixture contains exactly the same number of “A” and “B” reactive groups.

Critical Thinking Questions:

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

Yes, the reactions in Models 1 and 2 are stoichiometrically balanced. Both reactions start with 8 ‘A’ functional groups and 8 ‘B’ functional groups. Since the number of ‘A’ groups equals the number of ‘B’ groups, the reactions are stoichiometrically-balanced.

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:



Note: many students may draw one linear chain with an unreacted ‘A’ group on one end and an unreacted ‘B’ group on the other. This answer will still give them the correct N_n , but is not strictly the product that would result if the system reacted until no more reactions can take place. Ring formation may be worth a brief discussion since rings can be a side product in experimental step-growth polymerizations.

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

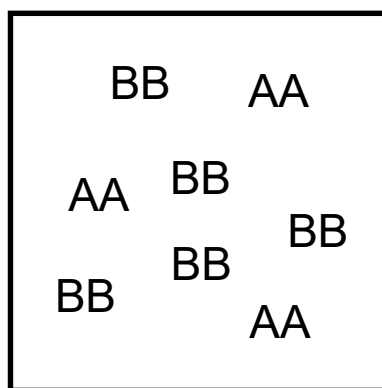
In both models, there is only one molecule in the final state.

Thus, for both models, $N_n = 8/1 = 8$.

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.

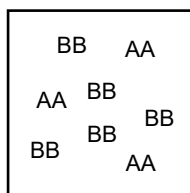
In this model, consider a reaction mixture that starts with 3 AA-type monomers and 5 BB-type monomers:



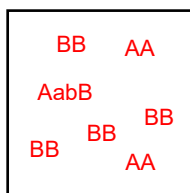
Step 0

Critical Thinking Questions:

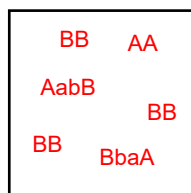
14. Fill in the blank spaces in the figure below with reasonable predictions for what the reaction mixture might look like in each successive step.



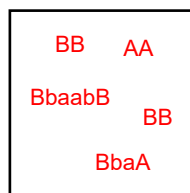
Step 0



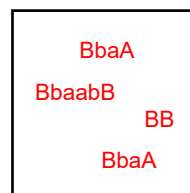
Step 1



Step 2



Step 3

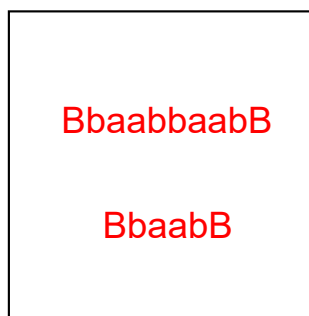


Step 4

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

Each step of the reaction uses up an equal number of ‘A’ and ‘B’ reactive groups. Since there are fewer ‘A’ groups in the initial reaction mixture, the ‘A’ reactive groups are the limiting reagent.

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:

There are two molecules in the final reaction mixture, so the number-average degree of polymerization is $N_n = 8/2 = 4$.

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?

N_n for the stoichiometrically-imbalanced reaction is *smaller* than N_n for the stoichiometrically-balanced reactions.

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

All of the chains have ‘B’ groups on the ends.

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.”

DEFEND: in a step growth polymerization, all of the molecules have either ‘A’ groups or ‘B’ groups on either end. If there is an excess of ‘B’ groups, the reaction will (ideally) go until all of the ‘A’ groups have been used up, leaving only ‘B’ groups on the ends of all of the polymer chains.

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:

	$p = 0.9$	$p = 0.99$	$p = 0.999$
$r = 0.9$	7	16	18.7
$r = 0.99$	10	67	166
$r = 0.999$	10	95	667

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.”

DEFEND: As we can see from the table in the previous question, achieving a large degree of polymerization requires *both* r and p to be close to 1. Since r reflects the reagent ratio, this means that we must measure the reagents very precisely to get as close to perfect stoichiometric balance as possible. Since p reflects the extent of reaction, or the fraction of reactive groups that have reacted, getting p close to 1 requires being able to push the $A + B \rightarrow ab$ reaction as far toward the products as possible.

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?

No, the same is not true for the stoichiometrically-imbalanced reaction in Model 3.

The key here is to realize that each step of the reaction does two things:

- a) it uses up one ‘A’ reactive group (and one ‘B’ reactive group, but we’re only counting ‘A’ groups here)
- b) it decreases the total number of molecules in the reaction by one (it takes two molecules and links them together to form one)

In Models 1 and 2, the stoichiometric balance means that the initial number of ‘A’ groups is equal to the initial number of molecules. In each step, both of the number of unreacted ‘A’ groups and the number of molecules decrease by one, so the number of ‘A’ groups is always exactly equal to the number of molecules.

In Model 3, however, the stoichiometric imbalance means that the initial number of ‘A’ groups is smaller than the initial number of molecules. While the number of unreacted ‘A’ groups and the number of molecules still both decrease by one in each step, they are not equal to each other since the initial values were not equal.

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 ?

Recall that, in general,

$$M_n = M_0 N_n$$

where M_0 is the molecular weight of a single monomer and N_n is the number of monomers.

Here, the molecular weight of the monomer is m_{AB} , so

$$M_n = m_{AB} N_n = \frac{m_{AB}}{1-p}$$

- 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?

To address this problem, we'll assume that on average, half of the monomers in each polymer chain will be AA-type monomers and half will be BB-type monomers (this is generally a reasonable assumption, except at very low degrees of polymerization).

In this case, the average number of AA-type monomers in a given polymer chain is $N_n/2$, so their contribution to the molecular weight is $m_{AA} \frac{N_n}{2}$. Similarly, the average number of BB-type monomers in a given polymer chain is also $N_n/2$, so their contribution to the molecular weight is $m_{BB} \frac{N_n}{2}$.

Put together, the total molecular weight is

$$\begin{aligned} M_n &= m_{AA} \frac{N_n}{2} + m_{BB} \frac{N_n}{2} \\ &= \frac{m_{AA} + m_{BB}}{2} N_n \\ &= \frac{m_{AA} + m_{BB}}{2} \frac{1}{1-p} \end{aligned}$$

Note that the second line of this expression looks a lot like $M_n = M_0 N_n$, but with $M_0 = \frac{m_{AA} + m_{BB}}{2}$. Thus, one way to interpret this result is to say that the number-average molecular weight is the number-average degree of polymerization times the *average* molecular weight of the monomers.

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?

Student 2 is correct. Because extra BB-type and Bx-type molecules both effectively terminate a chain end and stop it from growing, one Bx-type molecule has the same effect on the degree of polymerization as one BB-type molecule. As a result, the individual 'B' groups in the BB-type molecule are essentially half as effective as the single 'B' group in the Bx-type molecule, or, conversely, the 'B' group in the Bx molecule is twice as effective as each 'B' group from the BB-type molecules.

One way to see this is to consider the simple reaction of one AA molecule with two Bx molecules. In this case, when the reaction has gone all the way to completion, we should get a 'xbaabx' oligomer. This is essentially the same result that we would get from a reaction of one AA molecule with two BB molecules, which would result in a 'BbaabB' oligomer. In both cases we end up with the same final degree of polymerization, even though we had twice as many 'B' groups in the second case.

- 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.

As seen above, monofunctional molecules are very effective at capping polymer chains and preventing the reaction from going further. In a stoichiometrically-balanced reaction, if even just 5% of the 'B' groups come from monofunctional reagents, the average degree of polymerization will be capped at about 40 monomers, which is too short to be of much use in practical applications.