Molecular Weight Distributions in Step-Growth Polymerizations

Instructor Notes:

This activity introduces students to key concepts related to the molecular weight distributions obtained in step-growth polymerizations.

After completing this activity, students will be able to:

1. Calculate the fraction of polymer chains with length i in a step-growth polymerization,
2. Describe, qualitatively, the chain length distribution and how it changes with extent of reaction,
3. Calculate the expected dispersity for step-growth polymerizations, and
4. Explain why the limiting dispersity for a step-growth polymerization is 2.

Activity summary:

- **Activity type:** Learning Cycle
- **Content goals:** Molecular weight distributions and dispersity in step-growth polymerizations
- **Process goals:** written communication, critical thinking, information processing
- **Duration:** 25-30 minutes, including time for discussion
- **Instructor preparation required:** none beyond knowledge of relevant content
- **Related textbook chapters:**
  - *Polymer Chemistry* (Hiemenz & Lodge): section 2.4

Molecular Weight Distributions in Step-Growth Polymerizations

Model 1: Probabilities of Forming Different Chain Lengths

Suppose we perform a step-growth polymerization of AB-type monomers and stop the polymerization at extent of reaction p (i.e. we stop the polymerization when the fraction of A groups that have reacted is equal to p).

Suppose we then select a single molecule from this reaction mixture. This molecule will have an unreacted A group on one end, and an unreacted B group on the other.

Consider the following argument:

1. The unreacted 'B' group was originally part of an 'AB' monomer. Of these AB monomers ($i = 1$),
   - The fraction in which the A group monomer did *not* react, and the molecule remained an AB monomer, is $1 - p$.
   - The fraction in which the A group *did* react, and the selected molecule is at least an AbaB dimer, is p.
2. Of the molecules that reacted to form AbaB dimers ($i = 2$),
   - The fraction *of dimers* in which the A group did not react, and the molecule remained an AbaB dimer, is $1 - p$. The total fraction *of molecules* that are AbaB dimers is thus

     $$\begin{gathered}\text{(fraction of molecules that form dimers)} \cdot \text{(fraction of dimers that don't react further)}\\ = p(1-p)\end{gathered}$$

   - The fraction *of dimers* in which the A group did react, and the selected molecule is at least an AbabaB trimer, is p. The total fraction *of molecules* that form at least an AbabaB trimer is thus

     $$\begin{gathered}\text{(fraction of molecules that form dimers)} \cdot \text{(fraction of dimers that react further)}\\ = p \cdot p = p^2\end{gathered}$$

3. Of the molecules that reacted to form AbabaB trimers ($i = 3$),
   - The fraction *of trimers* in which the A group did not react, and the molecule remained an AbabaB trimer, is $1-p$. The total fraction *of molecules* that are AbabaB trimers is thus

     $$\begin{gathered}\text{(fraction of molecules that form trimers)} \cdot \text{(fraction of trimers that don't react further)}\\ = p^2(1-p)\end{gathered}$$

   - The fraction *of trimers* in which the A group did react, and the selected molecule is at least an AbababaB tetramer, is p. The total fraction *of molecules* that form at least an AbababaB tetramer ($i = 4$) is thus

     $$\begin{gathered}\text{(fraction of molecules that form trimers)} \cdot \text{(fraction of trimers that react further)}\\ = p^2 \cdot p = p^3\end{gathered}$$

Critical Thinking Questions:

1. Following this reasoning,

   a) How would you calculate the fraction of *molecules* that *remain* as AbababaB tetramers ($i = 4$)? Write your answer in both words and symbols.

   The fraction of molecules that remain as tetramers is

   $$\begin{aligned}&\text{(fraction of molecules that form tetramers)} \cdot \text{(fraction of tetramers that don't react further)}\\&= p^3(1-p)\end{aligned}$$

   b) How would you calculate the fraction of molecules that react further to form at least an AbababababaB pentamer ($i = 5$)? Write your answer in both words and symbols.

   The fraction of molecules that reacted to form at least a pentamer is

   $$\begin{aligned}&\text{(fraction of molecules that form tetramer)} \cdot \text{(fraction of tetramers that react further)}\\&= p^3 \cdot p = p^4\end{aligned}$$

2. Using the information in the model, and your answers to the previous question, fill in the following table:

i	Fraction of molecules that contain exactly i monomers
1	$1 - p$
2	$p(1 - p)$
3	$p^2(1 - p)$
4	$p^3(1 - p)$
5	$p^4(1 - p)$

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

The values acquire an additional factor of p for each additional monomer in the chain.

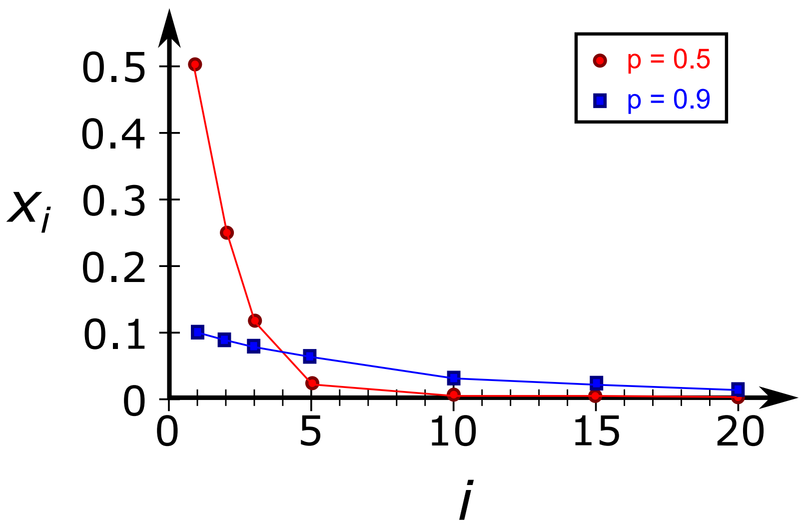
4. Complete the following statement:
"The fraction of molecules, x_i, that are composed of exactly i monomers is __________."

$x_i = p^{i-1}(1-p)$

5. 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	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

6. 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 $p = 0.9$.



7. 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.

   Both of these plots decrease exponentially toward zero with increasing values of i. However, the plot for $p = 0.5$ decreases much faster, and a higher fraction of the molecules have very short chain lengths, than in the case where $p = 0.9$.

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

   The most probable chain length is just the one with the highest value of x_i. Thus, the most probably chain length is $i = 1$ for both values of p.

9. 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.

   No, the fraction of chains with length $i + 1$ can never be greater than the mole fraction of chains with length i. This is because for each additional monomer, we pick up another factor of p; since p is always less than one, x_{i+1} will always be less than x_i.

   In mathematical terms, x_i decreases monotonically with increasing chain length i.

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

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

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 is a bit tedious, but if we do so, 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:

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

$$Đ = \frac{M_w}{M_n} = \frac{M_0 \frac{1+p}{1-p}}{M_0 \frac{1}{1-p}} = 1 + p$$

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

When $p = 0$, $Đ = 1 + 0 = 1$. This does make sense: when the extent of reaction is zero, no reactions have taken place, and the reaction mixture contains only monomers. Since all of the molecules in the mixture are thus identcail (and exactly the same size), the dispersity is 1 - the mixture is monodisperse.

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

When $p = 1$, DJ $= 1 + 1 = 2$. This is an important limit: the limiting dispersity for a step-growth polymerization is 2.

13. 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.

Following the argument presented in this exercise, no, the dispersity of a polymer produced by step-growth polymerization can never be greater than 2, because p can never be greater than 1.

Note for instructors: practically speaking, there are certain conditions that can generate dispersities greater than 2 (for example, when the reaction mixture contains multifunctional monomers that induce chain branching, or when the monomers are added in several batches - see DOI:10.1016/0032-3861(92)90340-3), but for the purposes of this activity, students should learn that the ideal limiting dispersity for step-growth polymerizations is two.

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?

$$p = Đ - 1 = 1.86 - 1 = 0.86$$

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

$$N_n = \frac{1}{1-p} = \frac{1}{1-0.86} = 7.1$$