# 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

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

   - 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

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

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

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

   - 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

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

## 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.

   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.

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 | |
| 2 | |
| 3 | |
| 4 | |
| 5 | |

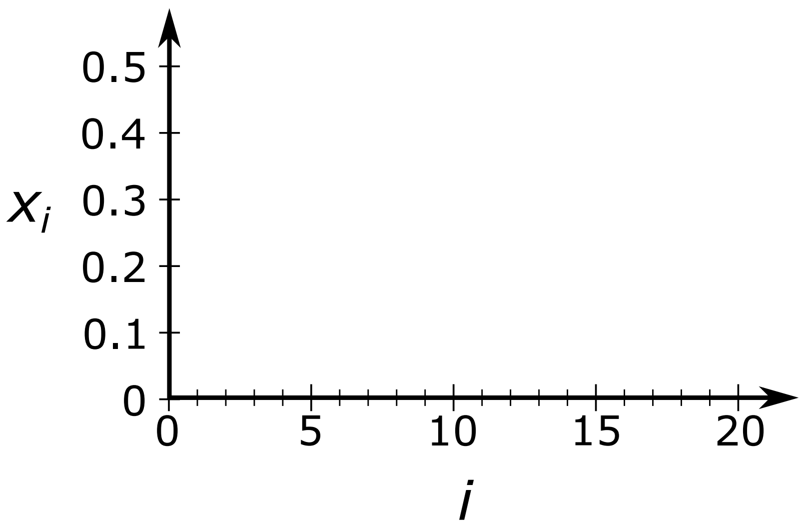
3. What pattern do you notice in these values? Briefly describe your observations in 1-2 complete sentences.

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

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 | | |
| 2 | | |
| 3 | | |
| 5 | | |
| 10 | | |
| 15 | | |
| 20 | | |

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.

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

## 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 $p$.

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

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

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.

**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?