Overview

There are two primary types of polymerization reactions, described broadly as follows:

Chain-Growth Polymerization	Step-Growth Polymerization
• Reaction adds repeating units one at a time to the chain.	• Molecules of any size may potentially react.
• High polymer is formed quickly.	• Molecular weight is low until a high extent of reaction has been achieved.
• Monomer concentration decreases steadily throughout the reaction.	• Monomer disappears early in the reaction.

During the polymerization reaction, the extent of reaction X varies from 0 to 1 and is defined as follows in each case:

$$X_{chain-growth} = 1 - \frac{number\ of\ unreacted\ monomer\ units}{initial\ number\ of\ monomer\ units} \tag{1}$$

$$X_{step-growth} = 1 - \frac{number\ of\ unreacted\ functional\ groups}{initial\ number\ of\ functional\ groups} \tag{2}$$

Consider a sample of polymer chains that contains N_i molecules of the i^{th} kind (different "kinds" meaning different molecular weights) and thus a total number of molecules $\sum_{i=1}^{\infty} N_i$. If each of the i^{th} kind of molecule has a mass M_i then the total mass of all the molecules is $\sum_{i=1}^{\infty} N_i M_i$.

The *number* average molecular weight of the sample is defined in Equation 3. This is simply the total mass divided by the total number of molecules. Number average molecular weights for commercial polymers are generally in the range of 10^4 to 10^5.

$$\bar{M}_n = \frac{\sum\limits_{i=1}^{\infty} N_i M_i}{\sum\limits_{i=1}^{\infty} N_i} \tag{3}$$

The *weight* average molecular weight is defined in Equation 4. Because larger molecules contribute more to $\bar{M}_w$ than smaller ones, $\bar{M}_w$ is always greater than (or equal to)$\bar{M_n}$.

$$\bar{M_w} = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \tag{4}$$

Many important polymer properties such as toughness, modulus, and viscosity are critically dependent on $\bar{M_n}$ and $\bar{M_w}$.

The quantity $\frac{\bar{M_w}}{\bar{M_n}}$ is the polydispersity and is a useful measure of the breadth of the molecular weight distribution curve. A polymer sample where all the chains are exactly the same length has a polydispersity of 1; proteins are a good example of polymers with polydispersities near 1. Typically, however, there is a broad distribution of chain lengths. The molecular weight distribution may be nicely shown by plotting $n(i) = \frac{N_i}{\sum_{i=1}^{\infty} N_i}$ as a function of i (this is the number fraction distribution) or plotting $w(i) = \frac{N_i M_i}{\sum_{i=1}^{\infty} N_i M_i}$ (this is the weight fraction distribution).

As an exercise, consider the collection of polymer chains illustrated in the Figure, where each circle represents a monomer unit. Assuming that each monomer unit has mass 1, demonstrate that:

$$\bar{M_n} = 4.3 \; ; \; \bar{M_w} = 4.8$$

Construct the plots $n(i)$ and $w(i)$.

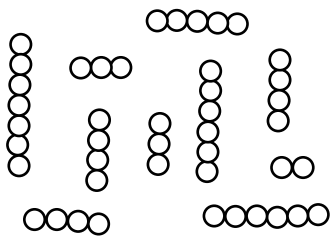

Figure 1: A polydisperse sample of chains.