Unlike simpler pure compounds, most polymers are not composed of identical molecules. The HDPE molecules, for example, are all long carbon chains, but the lengths may vary by thousands of monomer units. Because of this, polymer molecular weights are usually given as averages. Two experimentally determined values are common: \( M_n \), the number average molecular weight, is calculated from the mole fraction distribution of different sized molecules in a sample, and \( M_w \), the weight average molecular weight, is calculated from the weight fraction distribution of different sized molecules. These are defined below. Since larger molecules in a sample weigh more than smaller molecules, the weight average \( M_w \) is necessarily skewed to higher values, and is always greater than \( M_n \). As the weight dispersion of molecules in a sample narrows, \( M_w \) approaches \( M_n \), and in the unlikely case that all the polymer molecules have identical weights (a pure mono-disperse sample), the ratio \( M_w / M_n \) becomes unity.

\[
M_n = \sum v_i M_i \\
M_w = \sum v_i M_i^2
\]

\( v_i \) = mole fraction of chains with molecular weight \( M_i \) and \( M_i^2 \) = weight fraction of chains with molecular weight \( M_i \)

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