Molecular Weight

Nomenclature

The term molecular weight is commonly used to describe the mass of a polymer molecule. With the advent of advanced detection methods, the meaning of the term has become more obscure as the properties of individual molecules can now be observed. All elements have a defined mass dependent upon their isotopic composition. The ***atomic mass*** or less precisely the ***atomic weight*** of an element can be defined as the weighted average of all the naturally occurring isotopes using the carbon 12 scale and is given by the formula:

$$M_r = \frac{\sum_{i=1}^{i} A_i \cdot M_i}{\sum_{i=1}^{i} A_i}$$

Where A_i = Abundance of a specific isotope
M_i = Mass of a specific isotope

This can be contrasted with the ***monoisotopic*** mass which is the exact mass of the most abundant isotope of an element. [1]

Molecules (including polymers) are formed by bonding multiple atoms together. The ***relative molecular mass*** is equivalent to the atomic mass but it applies to molecules. It is obtained by summing the ***atomic mass*** of all of the atoms in the molecule. [2] The ***molecular weight***, ***molar mass*** and ***relative molecular mass*** are often used as synonymous terms to describe the weight or mass of a particular type of molecule. The ***molecular mass*** is synonymous to the ***monoisotopic mass*** of a compound and is specific for one isotope.

Polymers are large molecules formed using a repeating subunit. In most contexts, the molecular weight of a polymer refers to the ***relative molecular mass***. [3] The monoisotopic mass can also be determined in some cases. It is typically observed that monoisotopic composition is reserved for determinations made by LCMS while most other methods result in a *relative molecular mass*.

Polymer Molecular Weight

The term molecular weight as it is applied to polymeric materials implies something different from what is generally meant for small molecules. This is due to the fact that a polymer sample does not have a single molecular weight but rather a range of values (See Jordi white paper “Definition of a Polymer” for more information). In a given sample there may be polymer chains which contain widely different numbers of repeat units. In fact, most polymers contain some residual monomer (Degree of Polymerization “DP” = 1) and some chains which contain several hundred repeat units (DP > 100). These molecules will differ in *relative molecular mass* by several orders of magnitude.

For this reason, the molecular weight of a polymer is reported using averages. These averages are intended to describe the distribution of molecular weight values for the polymer chains. Three different molecular weight averages are commonly used to provide information about polymers. These are the ***number average molecular weight (M_n)***, ***weight average molecular weight (M_w)*** and ***viscosity average molecular weight.*** In addition, several other averages are used to lesser extents including the ***Z average molecular weight (M_z) and the Z+1 average molecular weight (M_{z+1})***. The averages are defined mathematically using the following formulas:

Number Average Molecular Weight = $\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i}$

Weight Average Molecular Weight = $\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$

Z Average or Size Average Molecular Weight = $\overline{M_Z} = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$

Viscosity Average Molecular Weight = $M_v = \left[\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i}\right]^{1/a}$

Where the summation is over all the chain lengths from i = 1 to I = ∞ and N_i is the number of molecules whose weight is M_i. [4] The viscosity average molecular weight also makes use of an additional term "a." This parameter is an empirical constant that is dependent upon the hydrodynamic volume or "the effective volume of the solvated polymer molecule in solution, and varies with polymer, solvent, and temperature." [4] It should be noted that M_v and M_w are the same when "a" has a value of 1.

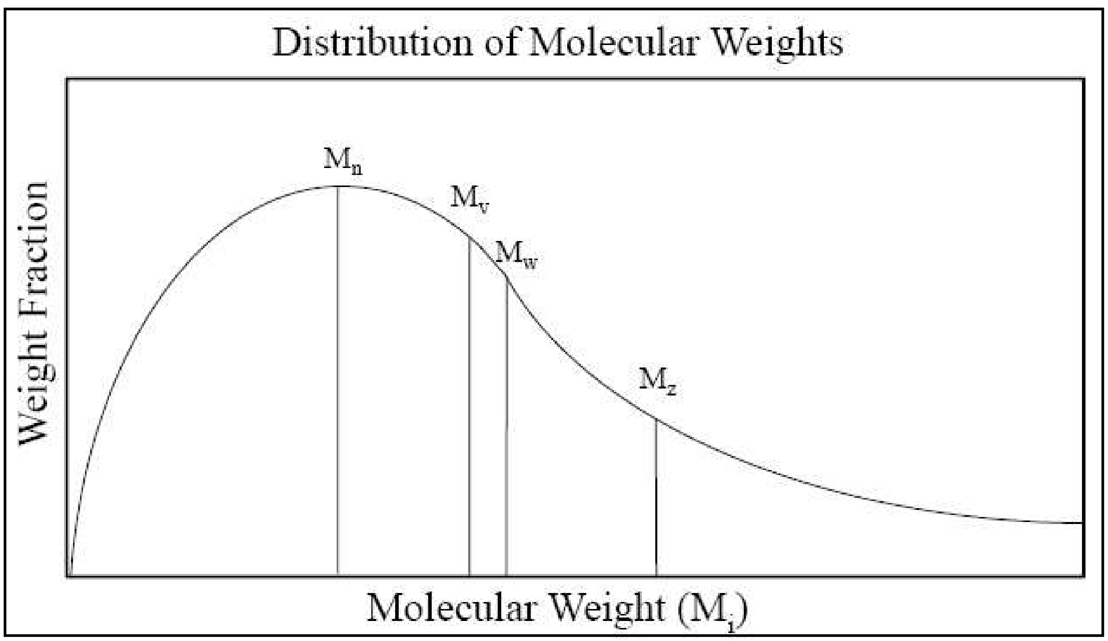

Figure I: Plot of the distribution of molecular weights in a typical polymer sample.

From the definitions of the molecular weight averages it can be observed that for a monodisperse polymer (polymers with chains of only one mass) the four averages are equal Mn = M_w = M_v = M_z. If however the polymer has many different sized chains (this is typically true) then the relationship between the averages is $M_n \leq M_v \leq M_w \leq M_z$. The presence of the additional M_i term in each succeeding average results in greater emphasis being placed on the highest molecular weight molecules. For step growth polymers which have a most probable distribution of molecular sizes the ratio of M_z:M_w:M_n is 3:2:1. [3]

To provide a reasonable estimate of the molecular weight, it is necessary to provide more than one average (unless the polymer is monodisperse). To fully describe the molecular weight distribution it is necessary to prepare a plot showing the weight fraction of the polymer chains which have a given molecular weight.

Figure I shows an example of a plot of the distribution of molecular weights in a typical polymer and the approximate location of the various averages on the curve.

Since most polymers are polydisperse, the four molecular weight averages are often used in conjunction with one another to define more thoroughly the nature of the molecular weight distribution. As can be seen from Figure I, M_n provides information about the molecular weight which is present at the greatest frequency in the sample. M_w is a weighted average which favors higher molecular weight molecules and appears on the high side of the molecular weight distribution. The M_z value has the term M_i to the third power and so it is even more skewed toward the highest molecular weights. The value for M_v ranges depending upon the constant “a” such that when “a” = 1 this average is equal to Mw. When “a” is less then 1, M_v is found to be between M_n and Mw. A typical value for “a” is between .5-.9. [4]

When polymers are provided for sale, the molecular weight reported is generally M_n or Mw. M_v is reported less frequently. In our experience, we have never seen the Z-average molecular weight listed apart from another average. This average is skewed too far out into the distribution to be a viable number to list individually.

Another parameter which is frequently used when describing polymers is the ***polydispersity index or PDI***. This parameter gives an indication of how broad a range of molecular weights are in the sample. The PDI is defined as:

$$PDI = \frac{M_w}{M_n}$$

The PDI can best be explained by looking at two polymers of the same molecular weight but with different PDI values. **Figure II** shows two theoretical polymer systems which have the same number average molecular weight (M_n). The two polymers differ from one another in that one polymer has a PDI of 1.1 and the second polymer has a PDI of 2.2.

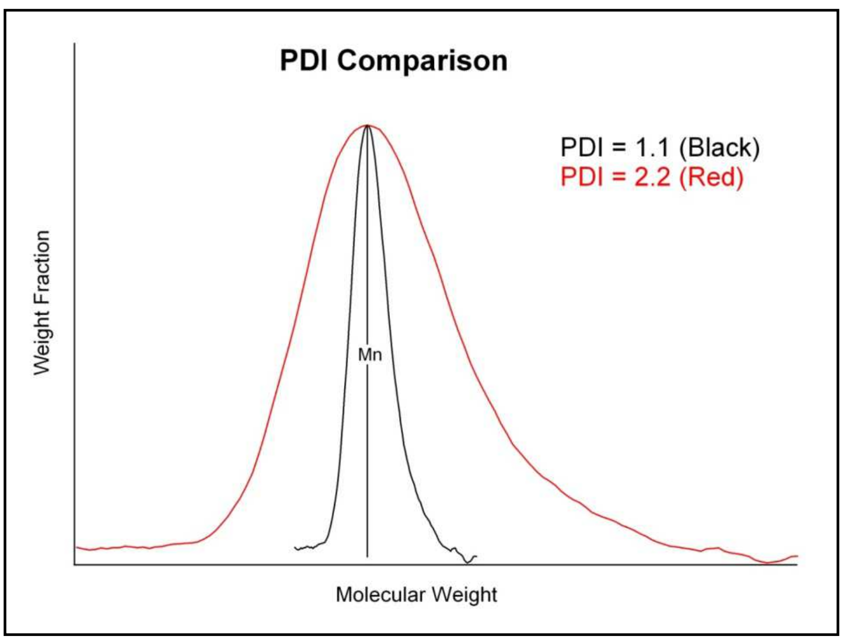

Figure II: Comparison of two theoretical polymer distributions. One polymer has PDI 1.1 (black) and a polymer of the same molecular weight with PDI 2.2 (red).

Molecular Weight Averages

To explain the meaning of the molecular weight averages, it is helpful to consider an analogy. Let's consider the average weight of a player on the offensive squads for two competing football teams. Now let's assume that these teams are identical accept for the weight of the center on each team. One team has a center who is 250 lbs and on the other team the center is 400 lbs. What effect will this have on the three types of averages? Figure I shows the players which make up the offensive squads of both teams. If we know the weights of the various players on each team, then we can calculate the number average (M_n), weight average (M_w) and Z-average (M_z) weights for the players on both teams. To begin, we will tabulate the data for each team in groups by their weights (Table I).

Table I		
Number of Players	Weight of Players Team 1	Weight of Players Team 2
Ni	**Mi**	**Mi**
2	100	100
6	150	150
2	200	200
1	250	400

Figure III: Offensive squad of a football team by player weight.

Table II summarizes the equations used to calculate each average and the resulting values for each team. To calculate the number average molecular weight (M_n), we take the sum of the weight of all the members of each team and divide it by the number of players on that team. This is the typical numerical average. We note that the M_n values for both teams are reasonably similar because most of the players have the same weights and M_n is not very sensitive to the largest members of the team.

$$M_n \, for \, Team \, 1 = \frac{(2 \cdot 100) + (6 \cdot 150) + (2 \cdot 200) + (1 \cdot 250)}{11} = 159$$

Number Average Weights	
Weight of Team 1	1750
Weight of Team 2	1900
Number of Players on each team	11
M_n Team 1	159
M_n Team 2	173
Percent Difference (Team 1 vs 2)	8%

In the number average, we saw that the weight classes (100, 150, 200, 250, 400 lbs) were weighted by the ***numerical fraction*** of the players of that weight. In the weight average, each different weight class is weighted by the ***weight fraction*** of players on the team who have that weight. The M_w values for both teams are then 170 and 208. The M_w values for the two teams differ to a greater extent than did the M_n values because M_w is more sensitive to the largest players. We note that the weight fraction contributed by the heaviest players can be large even if they are few in number.

$$M_w \; for \; Team \; 1 = \frac{(2 \cdot 100^2) + (6 \cdot 150^2) + (2 \cdot 200^2) + (1 \cdot 250^2)}{(2 \cdot 100) + (6 \cdot 150) + (2 \cdot 200) + (1 \cdot 250)} = 170$$

Weight Average Weights	
M_w Team 1	170
M_wTeam 2	208
Percent Difference (Team 1 vs 2)	20%

The difference between M_n and M_w can be better understood when one considers that on team one the total weight of the players which have a weight less than 170 is 1100 lbs (9 of 11 players) while those greater than this weight account for 650 lbs (3 players). Thus the three heaviest players on team one make up 37% of the total weight of team but only account for 27% of the people. Similarly on team two, the weight fraction of players above 208 lbs is 24% but the number fraction is only 9% (1 of 11 players). The presence of the one very large player on team two shifts the M_w average significantly toward higher weights. This demonstrates the increased sensitivity of the weight average to higher weight components.

Weight Fraction and M_w				
Team	Number Fraction of players < Mw	Weight Fraction of players < Mw	Number Fraction of players > Mw	Weight Fraction of players > Mw
1	73%	63%	27%	37%
2	91%	79%	9%	21%

Finally, we can calculate the Z-average molecular weight by introducing yet another term for the weight of each player. This is done by multiplying the number of players of each weight by their weight three times. This average strongly emphasizes the largest members of the team to the exclusion of the smaller players. The M_z values for the two teams were 181 and 259. From the values we note that the averages for both teams are in the following order $M_n < M_w < M_z$. This is always observed. Table II summarizes the results for all of the averages.

$$M_z \; for \; Team \; 1 = \frac{(2 \cdot 100^3) + (6 \cdot 150^3) + (2 \cdot 200^3) + (1 \cdot 250^3)}{(2 \cdot 100^2) + (6 \cdot 150^2) + (2 \cdot 200^2) + (1 \cdot 250^2)} = 181$$

Z-Average Weight	
M_z Team 1	181
M_zTeam 2	259
Percent Difference (Team 1 vs 2)	35%

Table II Summary of Weight Averages				
Average	Formula	Value Team 1	Value Team 2	% Difference
M_n =	$\frac{\sum_i^\infty MiNi}{\sum_i^\infty Ni}$	159	173	8%
M_w =	$\frac{\sum_i^\infty Mi^2Ni}{\sum_i^\infty MiNi}$	170	208	20%
M_z =	$\frac{\sum_i^\infty Mi^3Ni}{\sum_i^\infty Mi^2Ni}$	181	259	35%