Molecular Weight
There is more than one value

Nomenclature

The term molecular weight is commonly used to describe the mass of polymers such as polybutenes and polyisobutenes. 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.

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 the atoms in the molecule. 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.

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 or a distribution of values. 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.

- Number average molecular weight (Mn)
- Weight average molecular weight (Mw)
- Viscosity average molecular weight (Mv)

In addition, several other averages are used to lesser extents including the Z average molecular weight (Mz) and the Z+1 average molecular weight (Mz+1).

The averages are defined mathematically using the following formulas:

- Number Average Molecular Weight = $Mn = \frac{\sum N_i M_i}{\sum N_i}$
- Weight Average Molecular Weight = $Mw = \frac{\sum N_i M_i^2}{\sum N_i M_i}$
- Z Average or Size Average Molecular Weight = $Mz = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$
- Viscosity Average Molecular Weight = $Mv = \left[\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i}\right]^{1}/_{a}$

Where the summation is over all the chain lengths from i = 1 to I = ∞ and Ni is the number of molecules whose weight is Mi. 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'. It should be noted that Mv and Mw are the same when 'a' has a value of 1.

Rue de la Sablonnière 7
1000 Brussels
Belgium

ISO 9001 BUREAU VERITAS Certification

+32 2 219 48 11
sales@kematbelgium.com
www.kematbelgium.com

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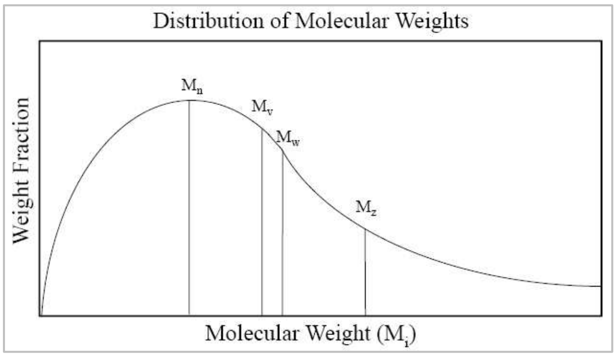

Figure I: Plot of the distribution of molecular weights in a typical polymer sample.

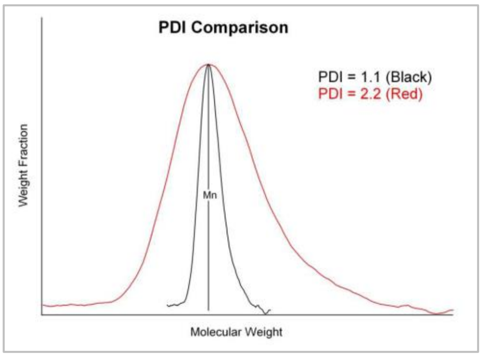

Figure II: Comparison of two theoretical polymer distributions. One polymer has PDI 1.1 (black) and a polymer of the same molecular weight with PDI 2.2 (red).

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 = Mw = Mv = Mz. If, however the polymer has many different sized chains, which is the case for polybutenes and polyisobutenes, then the relationship between the averages is Mn ≤ Mv ≤ Mw ≤ Mz.

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 polybutene and polyisobutene 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**:

- **Mn** provides information about the molecular weight which is present at the greatest frequency in the sample.
- **Mw** is a weighted average which favours higher molecular weight molecules and appears on the high side of the molecular weight distribution.
- The **Mz** value has the term Mi to the third power and so it is even more skewed toward the highest molecular weights.
- The value for **Mv** ranges depending upon the constant "a"; Mv is found to be between Mn and Mw.

The molecular weight for the Kemat PolybutTM polybutenes and Polybut HRTM polyisobutenes is generally expressed as Mn or Mw. Mv is used for our PolybolTM medium and high molecular weight polyisobutenes.

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 (Mn). 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.

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