A Question of Molecular Weight

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The molecular weight of benzene is 78. What is the molecular weight of a given sample of polymer, for example, of polystyrene? A polymer does not have a single molecular weight; we generally refer to a variety of molecular weight averages for a polymer, e.g., weight-average (Mw), number-average (Mn), and others.

Before we deal with polymers, let's ask ourselves, what is a molecular weight? What is the number that we refer to as molecular weight? Molecular weight, by the strict definition, is actually the weight, in grams, of Avogadro's number of molecules of a substance i.e., the weight of approximately 6 X 10^23 molecules. So, for instance, if we are talking about a substance like benzene, we can simply think of benzene as consisting of an assemblage of many of the same kind of molecules, all of them having the same size and weight. To obtain the "molecular weight" of benzene we simply add up the atomic weights of all of the atoms in the molecule. Since benzene contains six carbons we take six carbons and multiply by the atomic weight of carbon, 12, and obtain 72. We then take the six hydrogen's that are present in benzene and multiply by the atomic weight of hydrogen, 1 and obtain 6. The sum, 72 + 6, is then the molecular weight of benzene, 78. This is straight forward. But now let's extend the a little further. Let's ask ourselves what is the molecular weight of polystyrene once again, or of any polymer. Here we run into a problem because, if we had the ability to look at the molecules in a sample of polystyrene, we would find that we have a mixture of many different size molecules. And there is where the problem lies! How do you obtain the molecular weight of a mixture of materials that are all different form each other in terms of their sizes and weights? All polymers, with only a few exceptions, are mixtures of molecules having different molecular sizes and molecular weights and therein lies our problem. For a polymer, we use a "molecular weight average". We simply look at all of the different sizes of molecules and average them. The kind of molecular weight average we obtain depends upon the type of measurement used. And, this leads us to the number-average molecular weight, weight-average molecular weight, Z-average molecular weight, viscosity-average molecular weight, and others.

Analogy:

"STRAIGHT" Average vs. "WEIGHTED" Average

	CREDITS	GRADES
Math	5	80
English	5	80
French	5	80
Art	2	80
Music	2	80
Phys. Ed.	1	80
	20	

"STRAIGHT" Average: (80 + 80 + 80 + 80 + 80 + 80) ÷ 6 = 80

"WEIGHTED" Average: (5 x 80) + (5 x 80) + (5 x 80) + (2 x 80)+ (2 x 80) + (1 x 80) ÷ 20 = 80

Before we get into a discussion of how to calculate a molecular weight average for a polymer, let's take a look at an analogy, something I am sure you are familiar with. Think back to when you were in school. Suppose you were taking a program of courses such as Math, English, French, Art, Music, and Physical Education. Courses were worth different numbers of credits, depending on the relative difficulty of each course and upon the importance of the course in the curriculum. For example, let's assume that Math, English and French were worth 5 credits each, Art and Music, 2 credits each, and Physical Education only 1 credit, a total program of 20 credits. And let's assume that you were an "average" student; all of your grades were 80. To calculate a straight average, you simply add all of the grades for all the courses and then you divide by the total number of courses. This gives you an average of 80. Note that the average is identical to the grades when all of the grades are identical. In some schools, a different kind of "weighted" average is calculated; they recognize the fact that some courses are more difficult than others, some require more work and, thus, are more important. The grade for each course is multiplied by its corresponding number of credits, all of the products are added together, and the result is divided, not the number of courses, but by the total number of credits, In the case of the above example the result is again 80.

	Credits	Grades	Grades
Math	5	100	80
English	5	100	80
French	5	100	80
Art	2	80	100
Music	2	80	100
Phys. Ed.	1	80	100
	20		
	STRAIGHT Average	**90**	**90**
	WEIGHTED Average	**95**	**80**

If the grades for the courses were different from each other, then the weighted average and straight average would not be the same. Let's see what happens to the averages if we change some of the course grades. Let's assume that you are a fairly good student in Math, English, and French so that, instead of 80, you received grades of 100 in those three courses. Now, if we calculate a straight average we obtain not 80, but 90. However, the weighted average now becomes 95. Suppose you are not very good at Math, English, and French, but, rather, are outstanding in Art, Music and Physical Education. Let's give you a 100 in those three courses; note that the 100 in this case is given to the courses that are worth fewer credits, i.e., the "less important" courses. If we go through this exercise again the straight average is again 90. Note that in both cases we end up with the same straight average, the reasons being that when we calculate a straight average, all courses are given equivalent importance. But, when we calculate a weighted average, since we have the high, i.e., 100%, grades in the courses that do not carry as much credit, that are not as important, the result is a much lower weighted average than in the first case we discussed. In this case, the weighted average is only 85%. Note too, that in the original example, where all the grades were 80, the straight average and the weighted average were identical.

Now, keeping in mind what we have just discussed concerning a "straight" or "number" average vs. a "weighted" average, let's get back to molecules, molecular weight, and polymers. There are several reasons why there are different kinds of molecular weight averages for polymers. One of these reasons is that we end up with different kinds of molecular weight averages depending on the way in which we obtain the data, i.e., depending upon the type of physical or chemical measurement that is used to arrive at the molecular weight average. Let's take a look at some examples.

If we measure colligative properties of substances or the relative concentrations of end-groups in polymers then we obtain a molecular weight average in which all molecules are treated equally, i.e., are of equivalent importance. What do we mean by colligative properties? Certain properties of solutions are dependent only upon the numbers of molecular or ionic species present in the solution, and not upon their weights or sizes. These are called colligative properties, and include boiling point elevation, freezing point depression, vapor pressure depression, and osmotic pressure changes. All of these are used to measure molecular weights of substances, including polymers. End-group analysis, eg., hydroxyl number, carboxyl equivalent, etc., also lead to the molecular weight of a substance. The resultant molecular weight is analogous to the "straight" average discussed above, and is called the number-average molecular weight.

Colligative Properties
*** Osmotic Pressure**
*** Boiling Point Elevation**
*** Freezing Point Depression**
*** Vapor Pressure**

End-Group Concentration
*** Hydroxyl Number**
*** Carboxyl Equivalent**
*** Epoxy Equivalent, etc.**

$\searrow$ $\mathbf{M_n}$ $\swarrow$

THEY COUNT THE NUMBER OF MOLECULES OR EQUIVALENTS PER UNIT WEIGHT OF SAMPLE

All of these molecular weight methods count the numbers of molecules, or equivalents of a particular kind of group in the molecule, per unit weight of sample. All molecules are of equal importance when we measure colligative properties and end-group concentrations.

The number-average molecular weight is very sensitive to changes in the weight-fractions of low molecular weight species. Why is this so? For small molecules, a small weight of material represents a large number of molecules. For high molecular weight materials, a small weight of material represents only a very small number of molecules. The result is that, for low molecular weight materials a small amount of added material, by weight, makes a tremendous change in the number of molecules or particles in solution; so, the contribution to the number-average or "straight-average" is very large. Conversely, number-average molecular weight is relatively insensitive to similar changes in he weight of large molecules.

Another technique that is used to measure molecular weights of polymers is light scattering. A light shining through a very dilute solution of a polymer will be scattered by the polymer molecules. The scattering intensity at any given angle is a function of the second power of the molecular weight. Consequently, because of this "square" function, large molecules will contribute much more to the molecular weight that we calculate than small molecules. So, we obtain a "weighted" average as we did earlier in the analogy discussed above. It is called a weight-average molecular weight, and it is very sensitive to changes in number of large molecules in a given sample of a polymer.

LIGHT-SCATTERING MEASUREMENT

Scattering Intensity α **(Molecular Weight)^2**

$\searrow$ $\boldsymbol{M_w}$

LARGE MOLECULES CONTRIBUTE MOST TO SCATTERING INTENSITY

Dilute solution viscosities are routinely used to measure molecular weight. The rate at which a dilute solution of a polymer flows though a capillary is measured. What we are measuring then, is the frictional resistance to flow that result from the presence of different sized molecules of polymer in the dilute solution. What we are in fact measuring then, are the molecular sizes or the molecular volumes of the polymer molecules in the solution. The result is that the larger the molecules, the more interactions, and the greater will be the viscosity. The molecular weight average that we obtain by this technique is called the viscosity-average molecular weight. Large molecules contribute more to the viscosity-average than small molecules.

DILUTE-SOLUTION VISOSITY

Measures Molecular Size (Volume)

$\Downarrow$

$\mathbf{M_v}$

LARGER MOLECULES CONTRIBUTE MORE TO THE VISCOSITY

If a dilute solution of a polymer is subjected to a centrifugal field at a fairly low speed, we eventually establish a thermodynamic equilibrium where the molecules become distributed according to their molecular sizes. The molecular weight that we obtain from this experiment is called a Z-average molecular weight. The larger molecules are even more important in the case of the Z-average than the weight- or viscosity-average molecular weight.

CENTRIFUGATION

Establish thermodynamic equilibrium where molecules distribute according to molecular size

$\searrow$ $\mathbf{M_z}$

VERY LARGE MOLECULRES SETTLE MOST IN THE GRAVITATIONAL FIELD IN THE CENTRIFUGE

So far, we have looked at the reasons for different molecular weight averages in terms of the ways in which we obtain these averages, i.e., the experimental approaches through which we measure polymer molecular weight averages. Let's look at molecular weight average, now, from a different point of view. Let's see how different molecular weight averages are significant in terms of processing a polymer and in terms the properties of a polymer end-product. Let's examine such properties as tensile strength, hardness, flex life, stiffness, etc.

There is often a relationship between the properties of a polymer and the molecular weight average, but this relationship is sometimes a complex one. However, we often find that a given property is the direct result of, or, at least, is most influenced by either the very large or the very small molecules in a polymer sample. I say "most influenced" because all molecules contribute, in some way, to the physical and chemical properties of a substance.

If you are a manufacturer of polyethylene plastic bags, polypropylene rope, nylon fishing line, and other, similar materials where the tensile strength of the polymer that you are using is important, you would find, probably, that the tensile strength is a function of the weight-average molecular weight. Apparently, the tensile strength is often most influenced by the large molecules in the material.

TENSILE STRENGTH HARDNESS $\mathbf{M_w}$	$\mathbf{M_n}$ **BRITTLENESS-FLOW PROPERTIES**
FLEX LIFE STIFFNESS $\mathbf{M_z}$	$\mathbf{M_v}$ **EXTRUDABILITY MOLDING PROPERTIES**

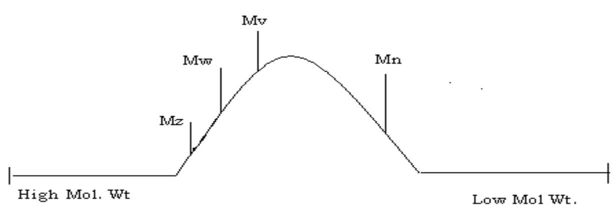
Let's assume now, that you manufacture plastic toll boxes of the kind that have plastic flexing hinges. In this case the flex life of the plastic is important to you. It has been found, in many cases, that the flex life is directly related to the Z-average molecular weight. The extremely large molecules are apparently most important in determining that property. You could monitor the quality of your incoming resin by measuring the Z-average molecular weight.

The brittleness of a polymer is often directly related to the levels of both the low and the high molecular weight species in a sample of polymer. However, we often add low molecular weight additives, i.e., plasticizers, to decrease the brittleness of a polymer. For example, phthalate esters are often added to polyvinylchloride in the manufacture of such products as plastic tubing, inflatable beach toys, etc. Another example, the addition of a low molecular weight polybutene oil as a plasticizer for polystyrene when manufacturing electrical insulators. We are in effect, "swamping out" the effect of the large molecules on the brittleness of the polymer by simply overloading the sample with very small molecules. Here, we often find a relationship between product quality and the number-average molecular weight. Thus, measurement of the number-average molecular weight provides insight into ultimate product quality. Let's go into just one more example.

Let's talk about the extrudability or the "moldability" of a polymer. We are concerned here with the ease with which a molten polymer can be made to flow through an orifice from an extruder into a mold and completely fill the mold. In this case, the viscosity-average molecular weight is important. The viscosity-average can be directly related to the processability when we consider extrusion and molding.

Since a polymer is generally a mixture of molecules of various molecular weights and molecular sizes, we can visualize a molecular weight distribution. If we plot the molecular weight distribution for a polymer and indicate the locations of the various molecular weight averages we have discussed, here is what we would see: The Z-average is located at the extremely high molecular weight end of the distribution, the weight-average slightly lower down in molecular weight; the viscosity average is very close to the weight-average. The number-average is located closer to the low molecular weight end of the distribution.

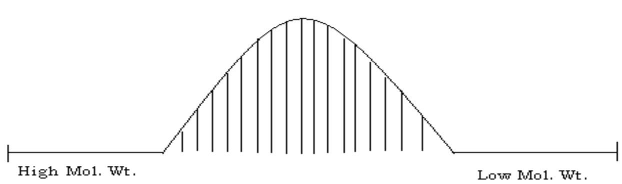
The narrower the molecular weight distribution of a polymer, i.e., the narrower the distribution of molecular weights of the components of a polymer, the closer the different molecular weight averages will lie to each other. Remember the analogy that we drew involving the course grades in school. When all of the grades where identical, i.e., when you received 80 percent in all six courses, the "weighted average" and the "straight average" were identical; a similar thing happens in polymers. If all of the polymer molecules in a polymer sample were of the same molecular size, then all of the molecular weight averages would be identical. Of course, this is never the case with commercial polymeric materials. But, polymer scientists and polymer technologists use this fact to calculate a number called "polydispersity", which is, essentially, a measure of width of the molecular weight distribution for a polymer. They calculate the ratio of weight to number-average molecular weight. The closer the polydispersity approaches a value of one, the narrower is the molecular weight distribution. Remember too, that the Z-average is always greater than the weight-average which, in turn, is greater than the viscosity-average, which is always greater than the number-average molecular weight. As we go in this series from number- to viscosity- to weight- to Z-average molecular weight, the large molecules in a polymer sample become increasingly important.



POLYDISPERSITY:

$$\frac{Mw}{Mn} > 1$$

USEFUL FOR ESTIMATING BREADTH OF A POLYMER DISTRUBTION



$$Mn = \frac{\Sigma H_i}{\Sigma(H_i/M_i)} \qquad Mv = \frac{(\Sigma H_i (M_i)^{\alpha})^{1/\alpha}}{\Sigma(H_i/M_i)}$$

$$Mw = \frac{\Sigma H_i M_i}{\Sigma H_i} \qquad Mz = \frac{\Sigma H_i M_i^2}{\Sigma H_i M_i}$$

CALCULATION OF MOLECULAR WEIGHT AVERAGES FORM GPC

Now, let's take a look at the various molecular weight averages from still another stand-point. Let's examine them in terms of the way in which we obtain them from GPC data. Here we see a molecular weight distribution for a polymer. It has been sliced into segments for the purpose of estimating the relative amounts of materials eluting in each molecular weight increment as shown. Hi represents the amount of polymer of a given molecular weight, Mi, eluting from the GPC columns. Now, looking at the equations that are used to calculate the various molecular weight averages, you will notice that as we go from number- to weight- to Z-average molecular weight, the molecular weights, Mi, are raised to increasingly higher powers; in other words, the higher molecular weight species become increasingly important. Now let's look at the equation for the viscosity-average molecular weight. The exponent, alpha, is the Mark-Houwink viscometric exponent, which can have values ranging from 0.5 to 1.0. For most polymers, in thermodynamically good solvents, the values actually range from about 0.7 to 0.9. An interesting property of this equation is that if alpha becomes 1.0 then the viscosity-average becomes identical to the weight-average molecular weight.

Let's summarize, now, what we have discussed:

1. Polymers are mixtures of molecules of various molecular weights and molecular sizes. Therefore, we must use molecular weight averages for these substances.

2. The type of average we obtain from various experimental measurements depends upon the physical or chemical property of the molecules involved in the measurement and upon the relative importance of large versus small molecules. Thus, measurement of colligative properties and end-group concentrations leads to calculation of a number-average molecular weight. Light scattering measurements result in a weight-average molecular weight. A Z-average molecular weight is obtained from centrifugation data; a study of the viscometric behavior of a dilute solution of a polymer leads to the viscosity-average molecular weight.

3. Various properties of polymers that are important in terms of their processability and their end-uses are directly related to specific molecular weight averages. This is because specific properties are primarily influenced by the levels of either high or low molecular weight species.

4. Different molecular weight averages are located at different points in a polymer's molecular weight distribution. If all of a polymer's molecules were identical, then all of its molecular weight averages would be identical.

5. The width of a polymer's molecular weight distribution is estimated by calculating its polydispersity, Mw/Mn. The closer this approaches a value of 1, the narrower is the polymer's molecular weight distribution.

6. The equations that are used to calculate the various molecular weight averages take into account the relative significance of different size molecules in these averages.