PART C

CHAPTER 8
MOLECULAR WEIGHT OF A POLYMER -
REFRACTIVE INDEX AND DENSITY

CHAPTER 9
DETERMINATION OF SPECIFIC
ROTATION OF OLIGOMERS FROM
MOLECULAR WEIGHT AND SPECIFIC
ROTATION OF MONOMER
CHAPTER 8

MOLECULAR WEIGHT OF A POLYMER - REFRACTIVE INDEX AND DENSITY
ABSTRACT

A general survey of the physical methods of evaluation of molecular weights is presented and the limitations are cited. In view of either laborious nature or the cost of equipment and limitations, a new method of evaluation of molecular weight from simple measurement of densities of monomers, polymers is presented. The results obtained are discussed critically in relation to the earlier available methods and the advantages of the present approach are outlined briefly.
8.1 INTRODUCTION

Molecular weight is one of the important parameters of a molecule which characterize the molecular activities. It has much significant role in the realm of stereochemistry of synthetic and biopolymers, because of its dependence on the size and shape of them. The determination of molecular weight is essential because the stereochemist need it for greater insight into the polymer.

A simple compound has fixed molecular weight. But the polymers are polydisperse in nature and therefore they have different molecular weights. The molecular weight of a polymer no matter by what method it is prepared will not have same values at all times. This is due to number of factors like their molecular degradation etc. that influence the polymerization. Important of all them is that chain termination is a random process and hence each polymer molecule can have different molecular weight. A polymer sample can therefore be thought of as a mixture of molecules of some chemical type, but of different molecular weights. In this situation the molecular weight of a polymer can only be viewed statistically and expressed as some average of the molecular weights contributed by the individual molecules. Different nomenclatures of molecular weights of polymers are in vogue though usually the method of calculating molecular weight averages of polymers are used.

**Different nomenclatures of molecular weights of polymers are:**

1. Calculation of the arithmetical mean or number-average molecular weight $M_n$. 
2. Calculation of weight average molecular weight $M_w$.

3. 'Z' average molecular weight $M_z$.

4. $(Z + 1)^{th}$ average molecular weight and

5. Viscometric molecular weight $M_v$.

$$M_s = \frac{\Sigma N_i M_i}{\Sigma N_i} \quad \text{(8.1)}$$

where $N_i$ represents number of molecules of molecular weight $M_i$.

To calculate the weight average molecular weight $M_w$, it is necessary to know the contribution of molecular weight of each component to the total molecular weight. The total molecular weight is equal to $\Sigma M_i N_i$ and hence the contribution of each molecular weight $X_i$ given by

$$X_i = \frac{N_i M_i}{\Sigma N_i} \quad \text{(8.2)}$$

Then

$$\bar{M}_w = M_1 X_1 + M_2 X_2 + M_3 X_3 + \ldots$$

$$= \frac{M_1 N_1 M_2}{\Sigma N_1 M_1} + \frac{M_2 N_2 M_3}{\Sigma N_2 M_2} + \ldots$$

$$= \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \quad \text{(8.3)}$$
In the case of a polymer which have poly-disparity $\overline{M_w}$ is always greater than $\overline{M_n}$.

$\overline{M_w} = \overline{M_n}$ in the case of a perfect homogeneous polymer.

Apart from $\overline{M_n}$ and $\overline{M_w}$ there are three other ways of expressing molecular weight based on sedimentation and flow behaviour of the polymer solution. They are $Z$-average molecular weight $M_{Z_1}$, $(Z + 1)^{th}$ average molecular weight and viscosity average molecular weight $M_v$. They are expressed as

$$M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \ldots \quad (8.3a)$$

$$M_{Z+1} = \frac{\sum n_i M_i^4}{\sum n_i M_i^3} \ldots \quad (8.4)$$

and

$$\overline{M_v} = \left[ \frac{\sum n_i M_i^{1+a}}{\sum n_i M_i} \right]^{1/a} \ldots \quad (8.5)$$

where 'a' is a variable ranging from 0.5 to 1 in the Mark Houwink equation which relates intrinisic viscosity ($\eta$) with viscosity average molecular weight $\overline{M_v}$. The light scattering, osmotic pressure, viscosity and ultra centrifugation technique are used to determine $\overline{M_w}, \overline{M_n}, \overline{M_v}$, and $M_z$ respectively. Some of the methods are given in brief here for the purpose of continuity. A consolidated list of methods of determination of molecular weights and their limitations$^1$ are given in Table 8.1.
### TABLE 8.1
Review of methods for determining molecular weight, size and shape of macromolecules

<table>
<thead>
<tr>
<th>No.</th>
<th>Method</th>
<th>Yields</th>
<th>M-range</th>
<th>Comments/Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Complete Chemical analysis</td>
<td>$M = \sum A_i$</td>
<td>No limit</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Quantitative chemical analysis of groups, the number of which is proportional to $M$ [g CO]</td>
<td>$M$</td>
<td>No limit</td>
<td>Knowledge of general chemical structure</td>
</tr>
<tr>
<td>3</td>
<td>(a) X-ray diffraction</td>
<td>Size, shape</td>
<td>No limit</td>
<td>3(a) Single crystal, heavy atom staining</td>
</tr>
<tr>
<td></td>
<td>(b) Neutron diffraction</td>
<td>Internal Structure</td>
<td></td>
<td>3(b) H atoms detectable.</td>
</tr>
<tr>
<td></td>
<td>(c) X-ray and neutron diffraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Electron microscopy</td>
<td>Size, shape</td>
<td>&lt;5000</td>
<td>Problems with radiation damage</td>
</tr>
<tr>
<td>5</td>
<td>Osmotic pressure</td>
<td>$M_n$</td>
<td>$10^4 - 10^6$</td>
<td>New technique. Vapour pressure osmometry</td>
</tr>
<tr>
<td>6</td>
<td>Viscosity of solutions</td>
<td>$M_{V}$ (size, shape)</td>
<td>$&lt; 10^7$</td>
<td>Structural effects</td>
</tr>
<tr>
<td>7</td>
<td>Diffusion</td>
<td>Size $M_{W}$</td>
<td>$&lt; 10^6$</td>
<td>Influence of structure solvation, concentration</td>
</tr>
<tr>
<td>8</td>
<td>Combination of 6 &amp; 7</td>
<td>$M_{w}$ shape</td>
<td>$&lt; 10^6$</td>
<td>New technique. Light scattering</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>See 6 &amp; 7</td>
</tr>
<tr>
<td>Method</td>
<td>M-range</td>
<td>Yields</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------</td>
<td>------------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sedimentation velocity</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;, size</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;, size, shape and M&lt;sub&gt;W&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combination of 7 &amp; 9</td>
<td>&lt;5x10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>No limit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrophoresis</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;, size</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;, size, shape and M&lt;sub&gt;W&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotational diffusion; fluorescence depolarization</td>
<td>No limit</td>
<td>No limit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow birefringence</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;, size, shape and M&lt;sub&gt;W&lt;/sub&gt;</td>
<td>M&lt;sub&gt;W&lt;/sub&gt;, size, shape and M&lt;sub&gt;W&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kerr effect</td>
<td>No limit</td>
<td>No limit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dielectric dispersion</td>
<td>M&lt;sub&gt;w&lt;/sub&gt;, M&lt;sub&gt;z&lt;/sub&gt;, Size M&lt;sub&gt;n&lt;/sub&gt;</td>
<td>M&lt;sub&gt;W&lt;/sub&gt;, Size M&lt;sub&gt;n&lt;/sub&gt;, Size M&lt;sub&gt;n&lt;/sub&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sedimentation equilibrium</td>
<td>&lt;5x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>&lt;5x10&lt;sup&gt;6&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light scattering 500 nm</td>
<td>&lt;10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>&lt;10&lt;sup&gt;5&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray small angle diffraction</td>
<td>a. X-ray small angle diffraction</td>
<td>a. X-ray small angle diffraction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b. Newton small angle diffraction</td>
<td></td>
<td>b. Newton small angle diffraction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As a rule $M_n < M_V < M_w < M_Z < M_z$, if all the $M_i$'s are the same, then all types of molecular weights will be equal.

There are different methods of determination of molecular weights of polymers (oligomers) prominent among them are a few physical methods which can be broadly divided into two classes; dynamic methods and static methods. Viscosity, osmotic pressure, diffusion, sedimentation and ultra-centrifugation methods are dynamic methods and light scattering and X-ray diffraction are static methods. These are essentially the methods used to evaluate molecular weights of polymers (or oligomers). There are a few more methods which are primarily meant to find out the size and shape of the molecules such as Rotational diffusion, flow birefringence etc. They are not discussed at present as the main stress is laid on the methods of determination of molecular weights alone.

8.2 METHODS OF DETERMINATION OF MOLECULAR WEIGHT

8.2.1 Osmometry

This method is widely used to determine number average molecular weight of polymers. If a pure solvent is separated from the solution by a semipermeable membrane the solvent molecules diffuse into solution. The flow of solvent can be stopped by applying appropriate pressure on the solution side. This applied pressure to stop the flow of the solvent through the semipermeable membrane into solution is called osmotic pressure. The osmotic pressure of a polymer is related to molecular weight $M_n$. 
A plot of \( \frac{\pi}{RTC} \) versus \( C \) gives a straight line.

If the graph is extrapolated to infinite dilution, the intercept gives \( \frac{1}{M_n} \).

To determine \( M_n \), the osmotic pressure of the solutions at several concentrations are measured. A graph is drawn and \( M_n \) is calculated.

### 8.2.2 Viscometry

Staudinger established an empirical relation between the viscosity of dilute solution and its molecular weight as

\[
\eta_{sp} = KMC 
\]

where

\( \eta_{sp} \) = specific viscosity of the solution

\( K \) = constant

\( M \) = molecular weight of dissolved polymer

\( C \) = concentration of a polymer in a solution.

However, the above equation is incorrect and does not relate the molecular weight with viscosity. For that reason a more popular empirical equation is

\[
[\eta] = KM^n
\]

... (8.9)
where

\[ \eta = \text{intrinsic viscosity} \]
\[ M = \text{molecular weight} \]
\[ \alpha = \text{constant characterising given polymer solvent system.} \]

Intrinsic viscosity is determined from the relative viscosity of the dissolved polymer solutions. Knowing this quantity the specific and reduced viscosities are calculated and a plot of \( \frac{\eta_w}{C} \) versus 'C' is made. The value of [\( \eta \)] is determined by extrapolating the graph to zero concentration. However, the molecular weight calculated is not always sufficiently accurate. Therefore this viscometric method is more suitable for determination of changes in molecular weights.

### 8.2.3 Diffusion

Diffusion is defined as directed thermal motion of molecules or very fine particles. This takes a place from the place where there are many to the place where there are few. As a result the concentration becomes uniform. The rate of diffusion \( \frac{dQ}{dt} \) is given as

\[
\frac{dQ}{dt} = -D \frac{dC}{dX} S \tag{8.10}
\]

'S' is cross sectional area and \( \frac{dC}{dX} \) is the rate of change in concentration with reference to distance and 'D' is known as diffusion constant. The concentration dependence of D is studied and the value \( D_0 \) is obtained extrapolating to zero concentration. Many of the polymers are found to follow the equation.

\[
D_0 = K_M M^b \tag{8.11}
\]
where $K_d$ is a constant for a given polymer solvent system. $b'$ is a parameter. This is also an empirical equation following Fick's second law.

### 8.2.4 Ultra Centrifugation

The particles which are in suspension settle down due to gravitational force. The macromolecules in a polymer solution also behave in the similar manner. But majority of the polymers form homogeneous solutions and counter the balancing diffusion effect as a result of which the molecules do not settle down. This is due to fast and random movement of the solute particles. If the gravitational force acting on the macromolecules is increased by some technique, the molecules can be sedimented. The increase of gravitational force is achieved by ultra centrifugation. The sedimentation velocity of the polymer molecules depends on the molecular weight. The ultra centrifuge can spin at about 65000 RPM. Due to the high centrifugal force, the molecules start sedimenting. By the application of Stokes law, the sedimentation coefficient '$S'$ can be related with molecular weight $M$ by the expression

$$M = \frac{S_0 RT}{D_0 (1 - \rho V)} \quad \ldots \quad (8.12)$$

where $D_0$ is a diffusion constant and can be determined as explained in the last section (8.2.3). The sedimentation constant $S_0$ can be computed by extrapolating the values of sedimentation constant for different concentrations to zero concentration to the equation.
Ks is a constant for a given polymer. \( V \) is the specific volume of the polymer and '\( \rho \)' the density of the solvent.

### 8.2.5 Light Scattering

In the case of polymer solutions, the polymer molecules are in the form of randomly coiled swollen chains and different regions of the macromolecular coil simultaneously and scatter the incident light beam. Thus different regions of same particle get exposed to the incident light having different phase. The result is that the scattered beam interfere with one another and hence intensity of scattered light diminishes when observed at an angle \( \theta \). The value of Rayleigh's ratio \( R_\theta \) varies with the observation angle \( \theta \). The final equation is given as

\[
\left[ \frac{KC}{R_\theta} \right]_{C \rightarrow 0} = \frac{1}{M} \quad \text{...} \quad (8.13)
\]

where \( C \) is the concentration and

\[
K = \frac{2 \pi^2 n^2 (dn/dC)^2}{\lambda^4 N^4} \quad \text{...} \quad (8.14)
\]

where '\( n \)' is the refractive index, \( dn/dC \) specific refractive index increment, \( \lambda \) is the wavelength and \( N \) the Avogadro number. A graph is drawn between \( \frac{KC}{R_\theta} \) and \( \sin^2 (\theta/2) + K_1 C \), where \( K_1 \) is an arbitrary constant. A double extrapolation
is employed i.e., $\theta \rightarrow O$ and $C \rightarrow O$. The coordinate intercept will give the value of $1/M$. This graph is called Zimm plot.

### 8.2.6 Small angle X-ray Scattering

The experimental techniques of small angle X-ray scattering has been improved to such an extent that the method can be used to get the information on size, shape and molecular weight of macromolecules (of molecular weight between $10^4$ to $10^7$).

Small angle X-ray scattering is similar to scattering of visible light with a difference in the wavelength which is one thousand times shorter. The size of macromolecules is greater than the above dimension. As a result, the X-rays are scattered. This scattered light fills the entire angle from $0^\circ$ to $180^\circ$. In small angle scattering, this angle is reduced to a small angle.

For the determination of molecular weight of a polymer a quantity known as absolute intensity is necessary. It is the fraction of $I_o$ and $P_o$ where $I_o$ is the scattered intensity and $P_o$ the primary intensity. The value of $I_o$ not only depends on $P_o$ but also on the molecular weight of the macromolecule and its concentration 'C' in the solution. $I_o$ is proportional to these quantities. Its value also depends on the contrast in electron density $\Delta Z$ between the solute and the solvent. The molecular weight of the polymer $M$ can be calculated directly from the following equation

$$M = \frac{I_o}{P_o F} \frac{a^2 10^3}{D (\Delta Z)^2 C} \quad \ldots \quad (8.15)$$
where

\[ a = \text{the distance of the sample from the registering plane in cm} \]

\[ F = \text{the area of the counter tube slit in cm}^2 \]

\[ D = \text{thickness of the cell used in cm and} \]

\[ K = \frac{1}{i_0 N} \quad \ldots \quad (8.16) \]

\[ i_0 = \text{the Thomson's constant, i.e. the scattering of the single electron and} \]

\[ N = \text{Avogadro number.} \]

A new technique of small angle X-ray scattering for the determination of molecular weight is proposed by Plestil et al. where by absolute intensity measurements are not necessary. The advantages and limitations of this new technique are discussed by them in detail.

The method of small angle X-ray scattering only suitable for the macromolecules of large size.

All the above methods are either very expensive or limited in their approaches. Most of the methods are laborious and time consuming. One other feature of utmost importance is that all the methods cited above require the density. A survey of literature on the molecular weight, density and refractive index of oligomers, in general and in ethylene glycols in particular, indicates that the variation of properties like density, refractive index with degree of
polymerization is almost in exponential fashion and then reach almost constant value after a particular value of polymerization.

The study on the density and refractive index of oligo methylenes; 2,1,1,1,2-oligo (formaldehyde) diacetates; and ethylene glycols confirm the exponential property (Figs. 8.1, 8.2, 8.3). The studies on the effect of polymerization on physical properties by Naryana Das also confirm this. Taking all these facts into consideration, it is felt whether an algebraic expression, though empirical in nature can be developed, which require only the knowledge of densities of monomers and polymers. Densities can accurately be measured by using a pyknometer with more easy one method of.

The present work is the outcome such investigations, and the application of such expression for the evaluation of molecular weights of polymers.

8.3 RELATIONSHIP

In the present work a new empirical relation between molecular weight of polymer and density is proposed, which reads as

\[
e^{-0.009 p} \frac{M_{\text{r}}}{M_{\text{m}}^{(0.77-0.001p)} M^{(0.23+0.001p)}} \left( \frac{M}{n^{0.77}} \right) = \Delta, \ \text{A constant} \quad \ldots \quad (8.17)
\]

where \(n, M\) refer to the refractive index and molecular weight of polymer and \(n_{\text{o}}, M_{\text{o}}\) refer to the refractive index and molecular weight of monomer. 'p' is a characteristic parameter called degree of polymerization.
Fig. 8.1. Exponential behaviour of density of oligo methylenes with molecular weight.
Fig. 8.2  Exponential behaviour of density and refractive index of oligo formaldehyde diacetates.
Fig. 8.3. Exponential behaviour of density and refractive index with molecular weight of ethylene glycol.
The value of 'p' can be evaluated from the equations given below

\[
\left( \frac{np}{n_0 p_0} \right)^{1.275} = e^{0.0008p} \quad \ldots \quad (8.18)
\]

where \( p \) and \( p_0 \) refer to densities of polymer and monomer.

For a monomer, equation (8.17), reduces to

\[
\frac{1}{M_0} \ln \left( \frac{M_0}{n_0^{3.4}} \right) = \Delta \quad \ldots \quad (8.19)
\]

The value of constant '\( \Delta \)' can be evaluated for the monomer of a macromolecule by knowing \( M_0 \) and \( n_0 \).

The same value of '\( \Delta \)' is used to evaluate molecular weight of polymer in equation (8.17).

This method is applied for the evaluation of molecular weight of polyvinyl chloride, poly styrene, poly methyl methacrylate, poly ethylene, poly vinyl acetate, poly arylonitrile and poly propylene.

The required data on the density and refractive index of the monomer, that of the polymer are taken from Ref. 5 and the molecular weight of the monomer is just compounded by adding the atomic weights of the atoms in the molecule given in Ref. 6 and are presented in Table 8.2. The values of \( p \), the polymerization parameter as calculated from the refractive index and density of the monomer and the polymer are given in Table 8.2. The calculated values of molecular weights of these polymers as obtained from equation (8.17) are also listed in Table 8.2. The
### TABLE 8.2

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>$M_o$</th>
<th>$\eta_e$</th>
<th>$\rho_o$</th>
<th>$n$</th>
<th>$\rho$</th>
<th>(p)</th>
<th>$M$(calc)</th>
<th>$M$(std)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly vinyl chloride</td>
<td>62.5</td>
<td>1.398</td>
<td>0.9918</td>
<td>1.5415</td>
<td>1.3840</td>
<td>687</td>
<td>$17.55 \times 10^4$</td>
<td>4.00 to 40.00 x $10^4$</td>
</tr>
<tr>
<td>Poly styrene</td>
<td>104.15</td>
<td>1.5468</td>
<td>0.9060</td>
<td>1.5950</td>
<td>1.0525</td>
<td>288</td>
<td>$9.44 \times 10^4$</td>
<td>1.00 to 400 x $10^4$</td>
</tr>
<tr>
<td>Poly methyl methacrylate</td>
<td>100.12</td>
<td>1.4142</td>
<td>0.9440</td>
<td>1.4920</td>
<td>1.1888</td>
<td>453</td>
<td>$16.45 \times 10^4$</td>
<td>1.00 to 700.00 x $10^4$</td>
</tr>
<tr>
<td>Poly ethylene</td>
<td>28.05</td>
<td>1.363</td>
<td>0.5660</td>
<td>1.4900</td>
<td>0.9334</td>
<td>939</td>
<td>$1.166 \times 10^3$</td>
<td>1.25 to 4.65 x $10^3$</td>
</tr>
<tr>
<td>Poly vinyl acetate</td>
<td>86.09</td>
<td>1.3959</td>
<td>0.9317</td>
<td>1.4657</td>
<td>1.1900</td>
<td>468</td>
<td>$15.2775 \times 10^4$</td>
<td>0.30 to 150 x $10^4$</td>
</tr>
<tr>
<td>Poly acrylonitrile</td>
<td>53.06</td>
<td>1.3888</td>
<td>0.8060</td>
<td>1.5180</td>
<td>1.1750</td>
<td>743</td>
<td>$16.452 \times 10^4$</td>
<td>6.00 to 30.00 x $10^4$</td>
</tr>
<tr>
<td>Poly propylene</td>
<td>42.07</td>
<td>1.3567</td>
<td>0.5139</td>
<td>1.4900</td>
<td>0.9050</td>
<td>1051</td>
<td>$17.38 \times 10^4$</td>
<td>2.20 to 7.00 x $10^4$</td>
</tr>
</tbody>
</table>
data on molecular weight of these polymers reported earlier and taken from reference 5 are also given in the same table.

8.4 RESULTS AND DISCUSSION

A glance of Table 8.2 reveal several interesting features. By and large the calculated values of molecular weights of the most of the polymers presented in this chapter are well within the range. The wide range in the values of molecular weights in the standard values indicate that there is no uniqueness in the values. This might be due to different conditions prevailing on the degree of polymerization and degradation. Notwithstanding this difficulty, the method can be claimed to be fairly successful as it provides an easy estimate of molecular weight.

Thus the new method of evaluation of molecular weight of polymers from simple measurement of densities and refractive indices, provides a less laborious and faster method of determination of molecular weight. Moreover the density and refractive indices, which are taken as measures of purity of the substance, so far, can also be made use of in the calculation of molecular weights of polymers. Thus this method provides a new approach of utilising the parameters, density and refractive indices, which involve relatively less expensive instrumentation for the evaluation of molecular weight. One more salient feature of this method is that it involves the parameters density (ρ) and refractive indices (n) only whereas any other technique within section 8.2 involves many more parameters besides n or ρ or both.

The extension of the applications of this method to other polymer systems is under progress at present.
REFERENCES


