Polymer Characterization: Polymer Molecular Weight Determination

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Polymers are large molecules consisting of a large number of small component molecules chemically linked together. They are made from constituent monomers through polymerization process. Polymers are unique materials in that they consist of a statistical distribution of chains of varying lengths, and each chain consists of monomer residues which affect its properties hence they require several parameters which need to be specified. Polymerization reactions produce a distribution of molecular weights and shapes. Polymer molecular weight could be expressed as number average molecular weight, weight average molecular weight, and polydispersity. Some of the most common methods for determining these parameters are colligative property measurements, light scattering techniques, viscometry, and size exclusion chromatography. Gel permeation chromatography is used to determine the number average molecular weight, weight average molecular weight, and polydispersity.

Keywords: Polymer; Molecular weight; Molecular weight distribution; Polydispersity; Gel permeation chromatography

1. Introduction

Polymers like simple molecules can dissolve in common solvents. They are composed of functional groups that are chemically reactive; they exhibit colligative properties and at specific wavelength can absorb energy. However, unlike simple organic molecules, they are made up of smaller monomer units of different sizes. These changes in the degree of polymerization, give rise to molecules with different molecular weights and different molecular weight distributions. Polymers can be characterized with respect to (i) chemical identity of the repeat unit, (ii) nature of the end group, (iii) nature and extent of cross linking, (iv) solubility, and (v) colligative properties.

Numerous methods abound for polymer characterizations and are classed under absolute (A), equivalent (E), and relative (R) (Table 1). Absolute methods allow the direct computation of polymer molecular weight from measured quantities without assumptions about the chemical and/or physical properties of the tested polymer molecule. The equivalent techniques, although direct calculation of polymer molecular weight can be made from measured data requires knowledge of the chemical structure of the polymer molecule. The relative methods, on the other hand, measured properties that depend on the chemical and physical structure of the polymer structure; requiring molecular weight curves of polymer standards of the same chemical and physical structure as that of the characterized polymer to be established.

However, all synthetic polymers contain polymer chain of uneven length; i.e they are polydispersed, and as such, molecular weight is not a single value but often described as average molecular weight. The average molecular weight can be expressed in different ways such as number average molecular weight (Mn), weight average molecular weight (Mw), viscosity average molecular weight (Mv), and higher average molecular weight (Mz, Mz+1). The choice of method for polymer molecular weight determination is influenced by factors such as (i) information required, (ii) operative region, (iii) cost effectiveness, and (iv) experimental conditions and requirements. Information on some of the techniques used for molecular weight determination is given in Table 1.

Table 1 Basic information regarding methods for polymer molecular weight determination.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Method</th>
<th>Type</th>
<th>Operative Region</th>
<th>Mean Molecular Weight Value Measured</th>
<th>Merit</th>
<th>Demerit</th>
</tr>
</thead>
</table>
| 1   | End Group Analysis                         | E    | < 10^5           | Mn                                  | It is cost effective                      | ➢ It requires known concentration
➣ Molecule-specific effectiveness is required                              |
| 2   | Ebullioscopy (boiling point elevation) and Cryoscopy (freezing point depression) | A    | < 10^4           | Mn                                  | They are cost effective                  | ➢ Require known concentration and large sample volume ➢ Have low resolution |
MK allows the graph of $\eta$ to be plotted from which the constants $K$, $a$, and $\alpha$ respectively, are obtained. The ratio of $M_z / M_n$ commonly referred to as polydispersity index measures the broadness of a molecular weight distribution in a polymer. For a monodispersed system where all the chains are equal, $M_w / M_n = 1$.

The viscosity average molecular weight ($\bar{M}_v$), on the other hand, is defined by Mark-Houwink equation [1]:

$$[\eta] = K \frac{M_v^a}{M}$$

where $[\eta]$ is the volume of polymer molecule in a given solvent (intrinsic viscosity), $K$ and $a$ are constants which describe the influence of solvent on the viscosity average molecular weight. The viscosity average molecular weight is not experimentally accessible and the calculation of the constants ($K$ and $a$) requires either the molecular weight ($M_n$ or $M_w$) of series of monodispersed polymers or $M_v$ of series of polydisperse polymers to be known aforetime. This allows the graph of $\log[\eta]$ versus $\log M$ ($M_n$ or $M_w$) to be plotted from which the constants $K$ and $a$ can be deduced from the intercept ($\log K$) and slope respectively.

An alternative method is the numerical method. In this method, the $M_v$ is replaced with $M_w$ and a polydispersity correction factor (pcf) is introduced [2] such that Eq. 5 becomes:

$$[\eta] = Kpcf\left(\frac{\sum NiMi}{\sum NiMi^2}\right)^{1/2}$$

### Table: Molecular Weight Distribution

<table>
<thead>
<tr>
<th>Method</th>
<th>Type</th>
<th>Range</th>
<th>Goal</th>
<th>Required Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osmometry</td>
<td>A</td>
<td>$10^8 - 10^6$</td>
<td>$M_n$</td>
<td>It is cost effective, requires known concentration, is less efficient for high molecular weight determination</td>
</tr>
<tr>
<td>Gel Permeation Chromatography (GPC)</td>
<td>R</td>
<td>$10^2 - 10^7$</td>
<td>Different values</td>
<td>It measures wide range of molecular weight, it is sensitive and has high resolution, it can measure polydispersity, it uses semi-dilute solution, it requires known concentration, it is slow, the equipments are expensive, sample solution is difficult to prepare</td>
</tr>
<tr>
<td>Light Scattering</td>
<td>A</td>
<td>$10^2 - 10^8$</td>
<td>$M_w$</td>
<td>It can measure polydispersity, requires known concentration, sample preparation is difficult</td>
</tr>
<tr>
<td>Sedimentation Equilibrium</td>
<td>A</td>
<td>$&lt; 10^6$</td>
<td>$M_n, M_z$</td>
<td>It can measure polydispersity, requires known concentration, sample preparation is tedious</td>
</tr>
<tr>
<td>Viscometry</td>
<td>R</td>
<td>$10^2 - 10^8$</td>
<td>$M_\eta$</td>
<td>It is cost effective, it measures wide range of molecular weight, requires known concentration, it shows low accuracy for low molecular weights</td>
</tr>
</tbody>
</table>

### 2. Molecular Weight Distribution

As noted in the introductory section, polymer chain distribution in synthetic polymers is always presented as average molecular weight calculated from the molecular weights of all the chains in the polymer sample. The number average molecular weight ($\bar{M}_n$), weight average molecular weight ($\bar{M}_w$), and higher average molecular weight ($\bar{M}_z$) are defined by the general expression:

$$\bar{M} = \frac{\sum NiM_i^a}{\sum NiM_i^{a-1}}$$

where $N_i$ is the number of polymer molecules, $M_i$ is the molecular weight, and the index ‘$a$’ takes positive integer. By setting $a = 1, 2, and 3$, the expressions for computing $M_n$, $M_w$, and $M_z$ respectively, are obtained.

$$\bar{M}_n = \frac{\sum NiMi}{\sum Ni}$$

$$\bar{M}_w = \frac{\sum NiM_i^2}{\sum NiMi}$$

$$\bar{M}_z = \frac{\sum NiM_i^3}{\sum NiMi^2}$$

The implication of these expressions is that $M_z > M_w > M_n$. The ratio of $M_w / M_n$ commonly referred to as polydispersity index measures the broadness of a molecular weight distribution in a polymer. For a monodispersed system where all the chains are equal, $M_w / M_n = 1$.
The \( pcf \) value depends on \( a, M_n, M_w, \) and \( M_z \); it can be calculated from Eq. 7 [2]:

\[
pcf = \left(\frac{M_w}{M_n}\right)^b \left(\frac{M_z}{M_w}\right)^c
\]

(7)

where \( c = 0.113957 - 0.844597a + 0.730956a^2 \)

\[ b = k_1 + k_2 \left[ \frac{M_z}{M_w} \right] - 1 \k_3 \]

(8)

where the constants \( k_1, k_2, \) and \( k_3 \) are least square polynomials function of \( a \):

\[
\begin{align*}
  k_1 &= 0.048663 - 0.265996a + 0.364119a^2 - 0.146682a^3 \\
  k_2 &= -0.096601 + 0.181030a - 0.84709a^2 \\
  k_3 &= -0.252499 + 2.31988a - 0.889977a^2
\end{align*}
\]

(9) (10) (11)

Authors have reported the success of this method in viscosity average molecular weight determination [3-5].

3. Methods of Molecular Weight Determination

3.1 Number Average Molecular Weight Determination

3.1.1 Osmometry Techniques

The two common osmometry techniques used for number average molecular weight determination are the membrane and vapour pressure osmometry. Vapour pressure osmometry is best suited for analyzing polymer samples with \( M_n < 20,000 \) g/mol. The limiting factor in membrane osmometry is the diffusion problem of low molecular weight molecules through the membrane.

Membrane osmometry depends to a large extent on the colligative properties of the polymer solution. These properties include osmotic pressure, boiling point elevation, vapour pressure reduction, and the freezing point depression. In this technique, polymer solution and pure solvent are separated by a membrane which is semi-permeable only to the solvent and not to the polymer (solute). Because the chemical potential of the pure solvent is higher than that of the solvent in polymer solution, the solvent moves from the pure solvent side to the polymer solution side. If there is an applied pressure, this movement can be hindered such that the there is no net flow across the membrane. In this condition, the applied pressure is equal to the osmotic pressure.

However, osmotic pressure of a solution is a function of molecular weight and concentration; hence Eq. 12 is usually used in the evaluation of number average molecular weight [1, 6].

\[
\frac{\pi}{c} = RT \left( \frac{1}{M_n} + A_2 c + A_3 c^2 + \ldots \right)
\]

(12)

or

\[
\frac{\pi}{c} = RT \left( \frac{1}{M_n} + \Gamma_2 c + \Gamma_3 c^2 + \ldots \right)
\]

(13)

where \( c \) is the concentration of the polymer in gram per unit volume of the solution, \( R \) is the universal gas constant, \( T \) is the absolute temperature, while \( A_2 \) and \( A_3 \) are virial coefficient expressed in mL mol/g² and measures the polymer-solvent interaction. \( \Gamma_2 = A_2/A_1 \) and \( \Gamma_3 = A_3/A_1 \). The derivation of Eq. 12 can be found in Ghosh [6]. In practice, the term in \( c^2 \) and those in higher powers of \( c \) are always neglected, as such, \( \pi/c \) is measured as a function of \( c \) at a particular temperature. A plot of \( \pi/c \) against \( c \) results in a graph with the virial coefficient as the slope and an intercept of \( RT/M_n \) from which the number average molecular weight can be derived.

The vapour pressure osmometry requires the use of thermoelectric method in the measurement of lowering vapour pressure since extreme sensitivity is needed for direct measurement. In thermoelectric method, two sensitive thermistors are placed in a chamber saturated with solvent vapour under a controlled temperature. Single drop of pure solvent is placed in each of the thermistors such that both the drops and the solvent have the same temperature. The drop in one of the thermistor is replaced with polymer solution; this creates temperature imbalance. Since the vapour pressure of the polymer solution is lower than that of the pure solvent, solvent molecules from the saturated phase condense on the polymer solution thermistor. As an effect, the temperature of the polymer solution increases until its vapour pressure rises and equals that of the pure solvent. Although, the temperature imbalance is small, it changes the resistance of the thermistors. A bridge circuit is used to measure the difference in resistance (\( \Delta R \)) of the two thermistors.

For a small value of change in temperature (\( \Delta T \)), \( \Delta T \propto \Delta R \). The working equation of vapour pressure osmometry (Eq. 13) [7] is similar to that of membrane osmometry and the same treatment given to the higher power of \( c \) in membrane osmometry is also applicable.
\[
\frac{\Delta R}{c} = \left( \frac{\Delta R}{c} \right)_{c \to 0} \left( 1 + \Gamma_2 c + \Gamma_3 c^2 + \ldots \right) \quad (14)
\]
where
\[
\left( \frac{\Delta R}{c} \right)_{c \to 0} = \frac{K}{Mn} \quad (15)
\]
and \(K\) is the calibration constant.

### 3.1.2 End Group Analysis

This method has presumed importance particularly in the determination of average molecular weight of step-growth polymers. Consider the step-wise condensation polymerization of polyesters:

\[
n\text{HOOC} - \text{R} - \text{COOH} + n\text{HO} - \text{R}^2 - \text{OH} \rightarrow \text{HOOC} - \text{R} - \text{CO} \left(-\text{O} - \text{R}^1 - \text{O} - \text{CO} - \text{R} - \text{CO} \right)_{n-1} - \text{O} - \text{R}^1 - \text{OH} + (n-1)\text{H}_2\text{O}
\]

Under the assumption that each polymer chain contains one \(-\text{OH}\) and one \(-\text{COOH}\) groups, direct measurement of the concentration of the groups can be done using chemical (titrimetric or pH measurement) or spectroscopic (infrared or nuclear magnetic) techniques. This is also applicable to other step-growth polymers. However, this method requires that the polymer be free of impurities and other groups present in the chain should not interfere in the determination of end group of interest.

For chain addition polymers in which the polymerization proceeds without measurable chain transfer, the use of End Group Analysis requires that the polymer is formed in the presence of a calculated dose of a strong chain transfer agent, such as a mercaptan, carbon tetrachloride or hydrogen sulfide [6]. If the polymer chain length is obtained by chain transfer, the number of polymer molecules may be related to the fragments of the chain transfer agent present in the polymer chain end. Actually, such chain transfer reaction would produce two chain ends; one due to the interception of the propagation process by the chain transfer reaction and the other resulting from re-initiation that follows the process. \(Mn\) may alternatively be calculated for chain addition polymer from a count of the initiator fragments occurring in the polymer, provided the mode of initiation and termination (i.e., combination or disproportionation) are known.

However, the major setback of this technique is the decrease in sensitivity with increasing polymer chain length. This method is restricted to polymer with molecular weight \(\leq 20,000\) amu. Aside this, it requires high concentration of polymer.

### 3.2 Weight Average Molecular Weight Determination

#### 3.2.1 Light Scattering Technique

This method is presumed most popular for the determination of weight average molecular weight \((\bar{M}_w)\). It allows polymer molecular weight and structure to be assessed. Fundamentally, if light passes through a medium, it scatters at different angles. This technique thus relies on the measurement of light scattered at an angle to the incident ray as it passes through the target. The intensity of scattered light incident on polymer sample is dependent of the polarity, chain size, and concentration; consequent upon this, light technique measures polymer molecular weight by quantifying the Raleigh scattering (elastic light scattering) from each polymer molecule. The measurement approach is simple as illustrated by the photomultiplier assembly in Figure 1. The scattering glass – cell is placed on a fixed center-tube and positioned at the center of an axis of rotation of a receiver photomultiplier tube assembly. The assembly is such that it can be rotated and fixed at a desired angular position during scattered light measurement. The famousness of this method stems from the fact that wide range of molecular weight (typically \(10^4\) to \(5 \times 10^6\) g/mol) can be determined.

The scattered light and the average molecular weight is related according to Eq. 16 [8]:

\[
\Delta R_\theta = K \bar{M}_w P(\theta) z (16)
\]

where \(\Delta R_\theta\) is the change in Raleigh scattering at a specified angle, \(\theta\), \(K\) is the optical constant, \(c\) is the polymer concentration, and \(P(\theta) z\) is the average particle scattering factor which accounts for the effects of measuring scattering from large molecules with relatively small wavelength.

However, the light scattering technique is deemed time consuming because it requires that the sample solution is completely free of dust and other impurities as these are capable of influencing the light scattering pattern. Also, as could be deduced from Eq. 16, change in Raleigh scattering is proportional to the sample concentration and molecular weight, hence this method requires high sample concentration to produce a detectable signal.
3.2.2 Sedimentation technique

Sedimentation technique is one of the classical methods for the characterization of polymers. Sedimentation equilibrium and sedimentation velocity are the two types; however, ultracentrifugation remains the analytical instrument for the two. This instrument measures sample concentration with respect to position from the center of a rapidly rotating cell.

In sedimentation equilibrium, the speed of a rotating motor in the centrifuge is adjusted so low that the forces of sedimentation and diffusion on polymer sample become comparable and allows equilibrium distribution of the sample particles to be established. Thus, equilibrium centrifuge uses gravitational potential to create a smooth but large concentration gradient. There is no solute transport in sedimentation equilibrium hence gives absolute value of average molecular weight. Although this technique is quite suited for aggregating and dissociating systems, it major demerit is the low speed required for equilibrium to be established.

The sedimentation velocity on the other hand is a transport technique which could provide information on the physical homogeneity of a sample, its conformation, interaction or co-sedimentation, and flexibility. It measures the rate at which particles are displaced under the influence of a strong centrifugal force. Sedimentation velocity is best suited for a monodispersed system but can still be applied for a polydispersed system.

The sedimentation velocity \( \frac{dr}{dt} \) is given by the equation [1]:

\[
S = \frac{1}{w^2 r} \left( \frac{dr}{dt} \right) \quad (17)
\]

where \( r \) is the distance from the center of rotation, \( w \) is the angular velocity, and \( S \) is the sedimentation constants. The sedimentation constant is related to the average molecular weight by the Svedberg equation given as [1]:

\[
M_w = \frac{RT}{(1-V)D} S \quad (18)
\]

\[
\frac{S}{D} = \frac{M_w + (1-Vc)}{RT(1 + M A_2 c + ...)} \quad (19)
\]

where \( D \) is the diffusion coefficient, \( V \) is the partial specific volume of the sample, \( e \) is the density of the solution, \( R \) is the molar gas constant, \( T \) is the absolute temperature, \( c \) is the concentration of the solution, and \( A_2 \) is the second virial coefficient.

3.3 Higher Average Molecular Weight Determination

3.3.1 Gel Permeation Chromatography (GPC)

GPC also known as size exclusion chromatography has become the preferred technique for the determination of polymer molecular weight in the 21st century because of its capacity to determine all the average molecular weights \( (\bar{M}_n, M_w, \bar{M}_z \text{, and } M_{w+1}) \) in a short time. This technique was first developed in 1964 by J. C. Moore [9] but has evolved greatly particularly in the areas of solvents used, column type and packing pattern, as well as detectors designs. The principle is typical of an ordinary chromatography. The GPC column makes use of a stagnant solvent which is present in pores of semisolid polymer materials whose structure is cross linked to form a gel and a flowing solution as the mobile phase. The mobile phase flows between the semisolid polymer materials and eludes in and out the pores of the
materials. Separation mechanism is essentially based on the differences in the size of polymer materials. In contrast to what is found in ordinary chromatography separation, large polymer molecules are separated first before the small size molecules. This is due to the fact that the large size polymer molecules cannot enter the pores easily and as such have the shortest retention time.

The separation parameters in GPC are derived from the distribution coefficient \( K_d \) which is related to the internal volume according to Eq. 20 [10]:

\[
K_d = \frac{V_{ai}}{V_i} = \frac{V_e - V_o}{V_o} \tag{20}
\]

where \( V_{ai} \) is the accessible internal volume, \( V_i \) is the internal volume, \( V_e \) is the elution volume, and \( V_o \) is the external volume. When \( K_d = 0 \), it implies that the molecules are excluded; \( 0 < K_d < 1 \) suggests that the molecules are retained in the gel pores while \( K_d = 1 \) means that the molecules occupy the total inner volume [10].

The schematic illustration of the modern GPC system is shown in Figure 2. The pump delivers the solvent onto the instrument at a constant rate and the autosampler inject sample automatically into the injection valve. The injection valve performs the task of injecting known concentration of sample into eluent stream. Separation takes place in the column and the detectors resolve components eluting from the column and as well measures the specific properties of the molecules. The computer, which is only a component of some modern GPC instrument automatically, calculates, records, and reports the numerical values of all the molecular weight averages. More so, information on the size and molecular weight dispersity can equally be obtained but this requires that standards of known size are run. Calibration curve can thereafter be made to determine the sizes of the unknown polymer sample.

The conventional GPC detectors cannot directly calculate the molecular weight averages of an unknown polymer sample rather the concentration of the eluting solution is recorded as a function of volume and the log (molecular weight) versus elution volume or elution time calibration of standards allows calculation of the molecular weight averages and molecular weight distribution of the test polymer sample as illustrated in Figure 3.

![Fig. 2 Illustration of the basic components of modern GPC.](image)
3.4 Viscosity Average Molecular Weight ($M_\text{ng}$) Determination

3.4.1 Viscometry

Polymers in general dissolve with difficulty in solvents than their corresponding monomers probably due to increased number of methylene group. When a polymer dissolves in a solvent, the viscosity of the solvent increases and polymer chain has direct influence. In 1930, Hermann Studinger reported a relationship existing between polymer molecular weight and the relative magnitude of increase in viscosity. The measurement of the viscosity of a solution is simple and inexpensive, although somewhat time consuming. The Ubbelohde capillary viscometer is commonly used for polymer solution viscosity determination. The polymer solution is introduced into the reservoir of the viscometer and aspirated to the upper bulb. Air is then admitted which causes the solution to flow down the capillary by gravity. For determination via this technique, the process is performed for pure solvent and polymer solution respectively. The solution flowing through the capillary obeys the Poiseuille’s law for laminar flow and implies that the pressure drop ($\Delta P$) varies as the viscosity ($\eta$) of the solutions [11]:

$$\Delta P = k \eta \quad (21)$$

$$k = \frac{8 RI}{\pi r^4} \quad (22)$$

From Eq. 21, the viscosity can be written as

$$\eta = \frac{\pi \Delta P r^4}{8IR}$$

where $r$ is the capillary radius (cm), $l$ is the length of the capillary (cm), $R$ is the volumetric flow rate through the capillary ($\text{cm}^3/\text{s}$).

The flow rate ($R$) will be inversely proportional to the solution flow time ($t$) if the bulb volume in the viscometer is fixed. However, $\Delta P$ is a function of solution density ($\rho$), hence

$$\eta = At\rho \quad (23)$$

where $A$ is a constant.

Equation 23 is valid only if $\Delta P$ is completely used up in overcoming viscous forces (i.e a dilute solution). If $t$ and $t_0$ are the flow rates and $\eta$ and $\eta_0$ are the viscosities of polymer solution and pure solvent respectively, the ratio $t/t_0 = \eta/\eta_0$. Since the lower limit of the relative viscosity ($\eta_r$) is unity, the specific viscosity ($\eta_{sp}$) which defines the relative increase in viscosity brought about by dissolved polymer molecules (Eq. 25) is considered more important [1].

The reduced viscosity ($\eta_{red}$) is obtained by relating $\eta_{sp}$ to concentration (Eq. 26). More so, the limit of $\eta_{red}$ at zero concentration gives the intrinsic viscosity, [$\eta$], (Eq. 27) while the inherent viscosity ($\eta_{inh}$) is the natural logarithm of $\eta_r$ divided by the concentration (Eq. 28). At $c = 0$, $\eta_{inh} = [\eta]$ hence $[\eta]$ can be obtained from any of the viscosities. The intrinsic viscosity is related to polymer molecular weight according to Eq. 5.

$$\eta_r = \frac{\eta}{\eta_0} \quad (24)$$

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \quad (25)$$

$$\eta_{red} = \frac{\eta_{sp}}{c} \quad (26)$$

$$[\eta] = \lim_{c \to 0} \frac{\eta_{red}}{c} \quad (27)$$

$$\eta_{inh} = \frac{\ln \eta_r}{c} \quad (28)$$

Fig. 3 Molecular weight determination (i) standard calibrated curve (ii) unknown sample.
3.5 New/Emerging Methods

3.5.1 Matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-MS)

Matrix-assisted laser desorption/ionization mass spectroscopy is relatively a new technique for the determination of polymer average molecular weight. Compared to other methods, MALDI-MS offered several advantages. Information on the average molecular weight and molecular weight distribution of narrow polydispersity (< 1.1) polymers can be obtained with high speed and precision [12, 13] and MALDI-MS technique requires small amount of solvent. Also, information on repeat unit, end-group structure, and chemical modification can be deduced by MALDI-MS, if oligomer resolution is attained [14]. However, the success of this technique is dependent on the availability of suitable standards with known molecular weights and molecular weight distributions. For the average molecular weight of a polymer to be determined accurately, the instrument and the sample preparation method have to provide a wide dynamic range of ion detection and true mass spectral representation of the relative intensities of oligomers in a polymer distribution.

Although MALDI-MS is not suitable for direct analysis of high polydispersity, when couple with GPC, accurate information can still be obtained.

3.5.2 Diffusion-ordered NMR spectroscopy (DOSY)

Li et al. [15] reported the first accurately measured average molecular weight of polymer by DOSY. This technique tends to separate the NMR signals of different species based on their diffusion coefficient. On the assumption that linear correlation exist between the logarithm of diffusion coefficient \((D)\) and the logarithm of molecular weight \((M_w)\) according to Eq. 29 [15], external calibration curves are made from which the molecular weight of narrow polydispersity polymers are predicted.

\[
\log D = df \log M_w + \log C \quad (29)
\]

where \(df\) is the fractal dimension of molecules and \(C\) is a constant.

4. Conclusion

For diverse reasons, particularly to have better understanding of a polymer system, characterization is essential. Different methods available for polymer molecular weight determination are outlined. The choice of method is dependent on the type of information required, operative region, cost, and experimental conditions.

References


