CHAPTER II

THE PHYSICAL METHODS IN CHARACTERIZATION OF POLYMERS
ABSTRACT

This chapter deals with a general introduction to the physical techniques used to characterise the polymers. The physical techniques presented are 1. Viscometry
2.1 Viscosity

2.1.1. Introduction

Generally physical methods are used for the determination of molecular weight as well as size and shape. The physical methods are osmotic pressure, light scattering, x-rays, Electron microscopy, Diffusion, sedimentation and viscosity etc., compared to these physical methods for the characterisation of macromolecules, the measurements of viscosity are simply performed on an inexpensive apparatus, and viscosimetry is unique because of the simplicity of the measurements, which is coupled with the relatively less difficulty of interpretation of the result. It allows the determination of the intrinsic viscosity of the protein molecule which is a complex function of its size and shape. This function has been evaluated theoretically for various model particles.

The magnitude of the intrinsic viscosity coupled with a knowledge of the molecular weight of the protein, enables a shrewd guess to be made of the modes particle which is most appropriate. Intrinsic viscosity and sedimentation constant often allows a correct choice to be made of the model
particle and evaluation of parameters. Thus, viscosity measurements find their major and continuing use in combination with other techniques.

Viscosity measurements give the following definite information.

1. If the intrinsic viscosity depends upon shearing stress, then the macromolecule is both very asymmetric and large and if it is a rod, this dependence can be used to determine its length and rotation diffusion coefficient.

2. If the plot of reduced viscosity against concentration shows upward curvature as the concentration is decreased, this is indicative of the presence of a charge flexible macromolecule.

3. A change in the viscosity of a protein solution as a function of time or some other variable indicates alternation of the shape and/or size of the protein due to a process such as denaturation or aggregation.

2.2.2. Definitions of Viscosity and its relations:

Viscosity is the property of a liquid whereby it tends to resist relative motion within itself. If different layers
of a fluid are moving with different velocities. Viscous forces come into play, tending to slow down the fast moving layers and to increase the velocity of the slower moving layers.

\[ F/A = \eta \frac{du}{dx} \]

where \( F/A \) is the shearing force per unit area and \( \frac{du}{dx} \) is the velocity gradient. If \( \eta_0 \) is the viscosity of the pure solvent and \( \eta \) is the viscosity of the solution then.

The relative viscosity is defined as the ratio of \( \frac{\eta}{\eta_0} \)

\[ \eta_{rel} = \frac{\eta}{\eta_0} = \frac{\text{Solution/Solvent}}{\text{Viscosity ratio}} \]

\( \eta_{rel} > 1 \)
where \( t \) and \( t_0 \) are the flow time of solution and solvent respectively.

The unit of viscosity as the poise

\[^{1}\text{degree sec. cm}^{-2}\]\

Detailed reference to viscosity can be found in the books of Naidu\(^2\), Leach\(^3\), Yang\(^4\), Tanford\(^5\), Moravetz\(^6\), Tanfaed\(^7\), Alexander Jhonson\(^8\), and Windells\(^9\).

The terms and symbols used in viscosity are given in table I.

The names are proposed by the International Union of pure and applied Chemistry (1952)\(^1\).

2.1.3 Measurement of Viscosity:

According to Newton’s law of viscous flow, the frictional force \( F \), that resists the flow of any two adjacent layers of liquids is given by

\[
F = \eta A \frac{du}{dx}
\]

When an external driving force is applied to overcome the frictional resistance and cause the liquid to flow uniformly throw a tube, the rate of flow is given by Hagen-Poiseuille (Van Wazer et al.)\(^10\) as
<table>
<thead>
<tr>
<th>Conventional name</th>
<th>Symbol</th>
<th>Definition</th>
<th>Name proposed by IUPAC</th>
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<tr>
<td>Viscosity of pure solvent</td>
<td>( n_0 )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Viscosity of Solution</td>
<td>( n )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Relative Viscosity</td>
<td>( n_{\text{rel}} )</td>
<td>( \frac{n}{n_0} )</td>
<td>Solution/Solvent viscosity ratio</td>
</tr>
<tr>
<td>Specific viscosity</td>
<td>( n_{\text{sp}} )</td>
<td>( \frac{(n-n_0)}{n_0} )</td>
<td>-</td>
</tr>
<tr>
<td>Reduced viscosity</td>
<td>( n_{\text{red}} )</td>
<td>( \frac{n_{\text{sp}}}{C} )</td>
<td>Viscosity numbers</td>
</tr>
<tr>
<td>Intrinsiac viscosity</td>
<td>([n])</td>
<td>( \lim_{c \to \infty} \frac{n_{\text{sp}}}{C} )</td>
<td>Limiting viscosity numbers</td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td>( \frac{n}{\rho} )</td>
<td>( \frac{n}{\rho} )</td>
<td>Viscosity /density ratio</td>
</tr>
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</table>
\[ n = \frac{\pi R^4 t \rho}{8 V L}. \]

Where \( V \) is the volume in milliliters of liquid of viscosity of \( n \) derived by the capillary of radius \( R \) Cm and length \( L \) Cm in time \( t \) seconds under a pressure head of \( \rho \) dynes/\( \text{cm}^2 \).

In capillary viscometers

\[ \rho = h \rho g \]

and normally decreases during the measurement of the flow time due to decrease of the hydrostatic head \( h \) of the liquid of density \( \rho \). 'g' is the acceleration due to gravity. The volume '\( dv \)' flowing through the capillary in time '\( dt \)' when the hydrostatic head is \( h \) and obtained by substitution and rearrangement of the above equation.

\[
\frac{dt}{\pi R^4 \rho g} = \frac{dv}{h},
\]

Integrating of this equation from the initial \( h_1 \) to the final hydrostatic head \( h_2 \) gives

\[
t = \frac{9 nL}{p \pi R^4 g} \int_{h_1}^{h_2} \frac{dv}{h} = \frac{K^1 n}{p},
\]
where \( K' \) is a constant for the particular capillary viscometers. By measurement of the flow time \( t' \) of a pure liquid of known viscosity and density, \( K' \) may be evaluated. Using this value of \( K' \) the viscosities of other unknown solutions are determined. Some of the Viscometers used generally are shown in fig.2.1

The empirical relationship between viscosity and solute molecular weight is shown

\[
[\eta] = KM^a
\]

where \( K \) is a constant and \( a \) is another constant. The value of which depends on the shape of the solute molecule, viz \( a=0 \) for spheres, \( a=0.5 \) for an ideal random coil, and \( a \approx 1.8 \) for long rigid rod. For a polymer whole \( K \) and \( a \) value have been determined empirically, the above eqn. provides a quick estimate of the molecular weight of a particular preparation and is specially useful for characterisation of synthetic polymers.

The constants \( K' \) and \( a' \) are determined by measurements of \([\eta]\) and \(M\) on samples of differing molecular weight of the one type of macromolecule in a particular solvent at a particular temperature. On the other method the shape of the solute particles can be determined by evaluating the value of \( a' \).
Fig: 2.1 Ubbelohde Viscometer.
Some more details on viscosity method to molecular structure can be obtained from the books of Jones and Talley, Larkins et al, Wada, Fugishige et al and Waisseberger.

2.2. Magneto-optic - Rotatory - Dispersion.

2.2.1. Introduction:

Various physical techniques are developed to investigate the macro molecular conformation. Among these physical methods one of the most widely used technique for the conformation of macromolecules is optically rotatory dispersion (ORD). ORD is used for the optical active molecules. By using magnetic field in conjunction with optical rotatory dispersion method, it should be possible to extend the scope of the method to all molecules whether the compounds are optically active or in active. This type of measurement is called magneto - optical - rotatory dispersion and has been the subject of a number of studies.

An important properties of normal optical rotatory power is that weak absorption bands often make as important, a contribution, to the optical rotation as strong absorption, bands, since the relevant parameter is the difference in the refractive index of the optically active system for the
two forms of circularly polarised light. In a similar way the refractive indices for right circular and left circular polarised light in any medium subjected to a magnetic field are different and it is this difference between the refractive index dispersion curves for the two forms of circularly polarised light that gives rise to the phenomenon of magneto optical rotation (Faraday effect).

Verdet explained the Faraday effect that, at a fixed wavelength, the optical rotation, was related to magnetic field, strength 'H' and the path length of the sample 'L' by the equation \( \theta = \frac{\gamma H L}{L} \), where \( \gamma \) a constant known as verdet constant.

Faraday effect has been observed in the radio wave, microwave, infrared, visible ultraviolet, and x-ray by several investigators in the respective fields.

Perkin first applied the magneto-optical rotation measurements to the elucidation of chemical structure. From his studies on organic compounds, he showed that the addition of CH\(_2\) group to a compound increases the molecular rotatory power by 1,023 units. His main conclusion is that chemical structure strongly influences magneto properties i.e. a comparison of results on magentic rotation
of related compounds can facilitate the elucidation of chemical structure.

Recently Dawber\textsuperscript{19} studied the magneto optical rotation in various concentrations of different solution and mixtures. Lefevre\textsuperscript{20} considered the usefulness of this technique on the evaluation of principal polarisability co-efficients of asymmetric non-polar molecule. Recently Rao et al.\textsuperscript{21} and Murthy et al.\textsuperscript{22} have attempted to see if molecular polarisability ($\kappa_M$) and magneto-optical-rotatory dispersion (MORD) could be used tools in conformations of the macromolecules. In this attempt to test the feasibility of using MORD in conjunction with ORD. In conformational analysis, an expression has been developed or magneto-optical rotation (verdet constant) in terms of refractive index ($n$). Rao and Murthy\textsuperscript{23} developed a method of evaluating mean molecular polarisability ($\kappa_M$) from vetdet constant. Starting from de Mallexman's principle and this expression is used as the basis for the derivation of equation for $\delta$ in terms of $n$. 
2.2.2. Recent Studies in MORD:

A review article on the Faraday effect, Pertington\textsuperscript{24} points out that aside from sporadic attempts to measure the rotation at different wavelengths, most of them work of the past 120 years is confined to measurements at the Sodium D-line wave length. Becquerel\textsuperscript{25} described some of the first dispersion measurements. In addition, magneto optic-rotation studies in the vicinity of the absorption bonds are discussed by Roberts\textsuperscript{26} and Stone\textsuperscript{27} for cerous sulphate and titanium, tetrachloride respectively. More recently, Eber Hardet\textsuperscript{28,29} et al. investigated the magnetic rotation spectra of certain diatomic molecules such as formaldehyde. Shashona\textsuperscript{30} investigated the general characteristics of magneto optic rotation spectra in the ultraviolet and visible regions near the absorption bonds of molecules and attempted to correlate spectral features with molecular structure. His dispersion measurements should that, there was similarly between magneto optical rotation and natural optical rotation.

He observed that there might be some possible structure for the excited state of molecule analogous to the asymmetric centre of natural optical activity. Moreover, the fact
that some absorption bonds are not magnetically active (i.e., no anomalous dispersion of magnetic rotation), indicates the possibility that cancellation of 'magnetic activity' may occur. This feature which he observed was compared to the loss of optical rotation properties for 'meso' configurations of naturally optically active molecules. He concluded that magneto-optical rotation may be useful for studying molecular structure and configurations. Foss et al. studies the magnetic circular dichroism, and they expected a relationship between the paramagnetism of a sample and its magnetic circular dichroism. Dowber tested the applicability of the one-term DRUDE equation for the solution specific rotation at the various concentrations and calculated the dispersion constants for LiCl, NaCl etc., and concluded that MOR data did impact give quite good linear plots. Dowber studied the excess magnetic relations of binary mixtures and he concluded that the magneto-optical method could provide useful complementary evidence to other techniques in understanding the structural properties of liquid mixtures.
2.3. **X-Ray Diffraction:**

23.1 **Introduction:**

X-ray diffraction can be used to study the determination of molecular symmetry and molecular parameters, in gases, liquids and solutions etc. In recent times somewhere between five and ten times as many molecular structures have been determined by means of x-ray diffraction as by all other experimental methods put together. Excepting in a small number of special uses, the molecular parameters obtained by x-ray diffraction are by enlarge, less accurate than those obtained by most other methods. Nevertheless, because of its wide x-ray diffraction is paramount importance for the determination of molecular symmetry and molecular parameter.\(^3\)

The present investigations are limited to polymers, in liquid solutions like glycols. Hence a brief account of the x-ray diffraction in liquids one can determine the intermolecular distances and hence the relation between the degree of polymerisation and inter molecular distance.
2.3.2. The theory and generation of x-rays

X-rays are produced when electrons with sufficient kinetic energy strike the atoms of any element. An x-ray tube consists of a filament or cathode and a metal target or anode. The filament, usually made of tungsten wire, is heated to produce a beam of electrons. The electrons are then accelerated by a high voltage and hit the target. The x-ray tube must be evacuated to prevent absorption of the electrons by gas molecules, and the target must be water-cooled, otherwise the electron beam would burn a hole in it. The x-rays pass out from the tube through windows which must be strong enough to hold a vacuum, but which must absorb x-rays only slightly. Since the absorption factor of atoms for x-rays increases with atomic number, the windows are usually made from thin sheets of beryllium or aluminium.

The resulting x-rays have a broad spectrum of wavelengths, but superimposed on this white radiation are a few sharp peaks of characteristic radiation. The latter as the name implies, are characteristic of the metal from which the target is made. It is possible to filter out all but one main peak called the K radiation, and x-ray diffraction...
experiments are almost always carried out with this highly monochromatic radiation. By appropriate choice of target material the wave length of x-rays may be varied, but the most commonly used metals are copper and molybdenum for which the wave length of the K radiation are 1.542 and 0.711 Å respectively.\[33\]

2.3.3. X-ray diffraction Studies in Non-Crystalline Materials

The degree of regularity on the atomic positions of substances is very small. Although a regular crystalline arrangement is not required for the production of diffraction effects as was first pointed out by Debye\[34\] in contrast to the sharp diffraction effects of crystalline materials it is found that liquids, glasses, resins, unoriented polymers etc. generate only one or more broad diffuse halos.

The monoatomic liquids and gases, the atomic environment about any reference atom is constantly changing, nevertheless, a small degree of less order results from the fact that two atoms cannot be separated by a distances smaller than the sum of two atomic radii. In molecular distances are introduced which are determined by the lengths of the bonds and any characteristic angles between them. A few
structural feature appears in glasses, resins, and un-oriented solid polymers, that is each atom possesses permanent neighbours at definite distances and indefinite directions although in general these vectorial properties relating an atom to its atomic environment are not the same for any two atoms in the assemblage.

As explained above a degree of local order prevails each in liquids, glasses, resins etc. as well as in the most minute fragments of a crystalline material. Accordingly it seems well to follow Bunns's stand point in characterising such substances as non-crystalline rather than amorphous. The term amorphous is to be considered synonymous with non crystalline.

Although the intensity scattering by a non crystalline material can be expressed as a function of any single angular variable such as $\theta$, $2\theta$, $\sin \theta$, etc. it is especially appropriate and useful to specify its dependence on $(\sin \theta/\lambda)$. The lack of structural regularity removes from the pattern any further differentiation of the scattering in a directional sense, and this has the direct consequence that the available intensity information permits the determination of the magnitudes of the interatomic vectors, but not their directions.$^{36,37}$
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