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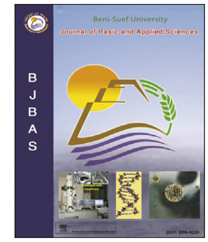

Full Length Article

Determination of scattering parameters of polyvinyl alcohol by static laser scattering

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H. Hashim*, **F. El-Mekawey**, **H. El-Kashef**, **R. Ghazy**

Laser Laboratory, Physics Department, Faculty of Science, Tanta University, Tanta 31527, Egypt

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ABSTRACT

Static laser scattering (SLS) is one of the most efficient techniques used for the molecular weight determination of polymer. Among of all polymers, polyvinyl alcohol (PVA) polymer was selected. A polystyrene (PS) was used as a standard polymer. A polyvinyl alcohol was investigated for its importance in pharmaceutical, biomedical, and industrial applications. Different concentrations in the range (3–9) $\times 10^{-3}$ g mL^{-1} were prepared. SLS data were obtained by using a self-built of the laser scattering system. The angular behavior of those selected polymer solutions with different concentrations were studied by plotting the intensity of the scattered light against the scattering angle in the range of 40–140°. By using Zimm plot the weight-average molecular weight $\mathbf{M_w}$, radius of gyration $\mathbf{R_G}$, and second virial coefficient $\mathbf{A_2}$ of the standard PS and PVA were determined.

1. Introduction

A polyvinyl alcohol is a popular polymer its density 1.26 g/ml at 25 °C and its glass transition temperature 85 °C. This polymer is used as relief of symptoms of dry eye and artificial tears, paper, Wood Processing, and Building Industry. The chemical formula of polyvinyl alcohol is shown in (Fig. 1).

Scattering method is one of the most accurate techniques for the determination of polymer's molecular weight. Measuring scattering from large solute molecules with a relatively small wavelength. The strength of this technique; it is a quite sensitive, has a wide range of molecular weight determination, typically from about 10^4 to 5×10^6 g mol^{-1}, absolute method that does not need calibration, and can give the radius of gyration and the second virial coefficient (Li, 2008; Stevens, 1998).

The different concentrations of the polymer solution give different refractive indices. As a result of the fluctuation in refractive index; the incident light will be scattered by each illuminated macromolecule in all directions.

The basic parameters yielded by light scattering measurements of a dilute polymer solution are the weight-average molecular weight, radius of gyration, and second virial coefficient, for large molecules.

The phenomenon of the light scattering from dilute polymer solution is based on rigorous theory, which is a combination of physical optics and thermodynamics (Brown, 1996).

* *Corresponding author.*
E-mail address: Prof_hmh@yahoo.com (H. Hashim).

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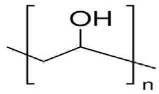

Fig. 1 – Chemical formula of polyvinyl alcohol polymer.

The theory is rather complex, as testified by the fact that it was developed by no lesser personages than Einstein and Debye. In the theory of light scattering the concept of small and large particles is important.

Small particles are meant particles or macromolecules, which are much smaller than the wavelength of incident light. Such particles behave as a point source of scattered light. In experimental practice, particles smaller than (λ/20) of light can be treated as small particles, and particles larger than (λ/20) of light called large particles (Ghazy, 2011).

Therefore, the scattering of visible light is one of the fundamental experimental techniques of the physical chemistry of polymers. In the mood of what is called, the classical or static laser scattering (SLS), which is known as Rayleigh scattering.

In the present work we had built a laser scattering system by which we had measured the angular distribution of the scattered laser light. From these data we had determined the weight-average molecular weight $\mathbf{M_w}$, radius of gyration $\mathbf{R_G}$, and second virial coefficient $\mathbf{A_2}$. The selected polymers are polyvinyl alcohol and, our system standard by polystyrene.

Light scattering in case of small particles, the average Molecular weight of polymer can be determined from its contribution to the overall intensity of light scattered from its dilute solution. This contribution equals the difference between the scattered intensities of the solution and pure solvent. In order to eliminate the influence of specific experimental conditions, such as intensity of the incident beam, its polarization, the geometry of the apparatus, a quantity for the normalized scattered light intensity, called the Rayleigh Ratio of symbol (R_θ) has been defined. The subscript (θ) denotes the angle at which the scattering intensity has been measured. At infinite dilution, the intensity of light scattered from a solution of uniform small macromolecules is described by the simple Equation (Sun, 2004):

$$\frac{kc}{R_\theta} = \frac{1}{M_W} \tag{1}$$

where c is the concentration of the solute, M_w is the weight-average molecular weight, and k is the optical constant (Sperling, 2006) and is defined as:

$$k = \frac{2\pi^2 n_o^2 \left(\frac{dn}{dc}\right)^2}{\lambda^4 N_A}\left(1+\cos^2\theta\right) \tag{2}$$

where:

n_o: the refractive index of the solvent,
λ: the wavelength of the incident light in vacuum,
N_A: Avogadro's number; and
dn/dc: the specific refractive index increment.

The value of k depends on the polymer, solvent, and temperature. For highly dilute solutions, the differential ratio can be replaced with no loss of accuracy by the ratio (Δn/c), which is a quantity easy to measure, where Δn is the difference between the refractive indices of the solution and solvent.

With molecular solutions, the colloidal particles consist of small gel particles, i.e., the coiled chain molecules which have become solvated with solvent to extent that the entire gel particles consist of 90–99 % of solvent. In this case, the refractive index of the solution differs slightly from the solvent's refractive index. This gives rise to simple physical laws for the scattering of light (Siddiq et al., 1997; Siddiq and Wu, 1997).

The basic equation which describes the light scattering from dilute solutions of no uniform small macromolecules according to P. Debye is usually written as:

$$\frac{kc}{R_\theta} = \frac{1}{M_W} + 2A_2c + \left(3A_3c^3 + \cdots\right) \tag{3}$$

where A_2 and A_3 are the second and third virial coefficients respectively (Sun, 2004) and:

$$R_\theta = \frac{I_\theta r^2}{I_0 V} \tag{4}$$

where:

I_θ: the scattered intensity,
I_o: the incident intensity,
r: the distance between the sample and detector; and
V: the scattering volume.

The second virial coefficient is an important thermodynamic characteristic of the polymer-solvent system. High values of A_2 are characteristic of system with intense interaction between the polymer and solvent, that means of a good solvent for the given polymer.

To determine the molecular weight of a polymer which has molecules smaller than λ/20 (where λ is the wavelength), we measure the intensity of light scattered from two to four solutions with different concentrations, calculate the ratio kc/R_θ, most frequently kc/R_{90} and plot them as a function of polymer concentration. The intercept with the axis of ordinatesmgives the reciprocal value of M_w according to Eq. (1) (Shere et al., 1996) and the slope of the concentration dependence being twice the value of A_2.

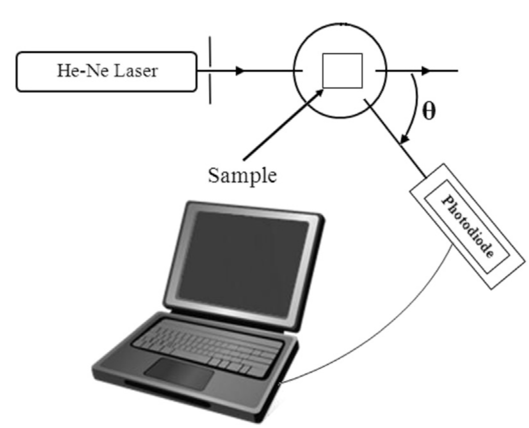

Fig. 2 – Schematic diagram of static laser scattering (SLS) measurement experiment set-up.