Static Light Scattering and Zimm Plot Activity

Static light scattering (SLS) measures the time-averaged intensity of light scattered by macromolecules or aggregates in solution. Typically, SLS measurements are taken at multiple solute concentrations, multiple angles, or both to allow the determination of the weight-averaged molecular weight (M_w), the "radius of gyration" (a measure of how the mass is distributed around a particle's center of mass), and the second virial coefficient (a measure of macromolecular self-association). The governing equations for static light scattering experiments are:

$$\frac{K\,c}{R_{EX}}=\left(\frac{1}{M_w}+2\,A_2\,c\right)\left(1+\frac{q^2R_g^2}{3}\right) \tag{1}$$

$$K=\frac{4\pi^2 n_0^2\left(\frac{dn}{dc}\right)^2}{N_A\lambda^4} \tag{2}$$

$$q=\frac{4\pi n_0}{\lambda}\sin\left(\frac{\theta}{2}\right) \tag{3}$$

where n_0 is the refractive index of the solvent, λ is the wavelength of the incident light, N_A is Avogadro's number, A_2 is the second virial coefficient, c is the solute concentration in solution, dn/dc is the refractive index increment of the solute in the solution, R_{EX} is the excess Rayleigh ratio between the macromolecular sample and the pure solvent at an angle θ, q is the scattering vector, and R_g is the radius of gyration.[1,2] After performing a series of measurements at varying angles and varying concentrations, (Kc/R_{EX}) is plotted as a function of solute concentration (c) and scattering angle (θ) to give a Zimm plot as shown in Figure 1. The value of S is chosen to sufficiently space the data points to produce a well-spaced plot. The experimental data for varying concentrations (Figure 1, blue dotted lines) and for varying angles (Figure 1, red dashed lines) are extrapolated to zero concentration and zero angle (Figure 1, green solid lines). The intercept of the c = 0 and the θ = 0 lines is the reciprocal of the weight-averaged molecular weight ($1/M_w$). The R_g of the solute is determined from the slope of the c = 0 line and the second virial coefficient is determined from the slope of the θ = 0 line.

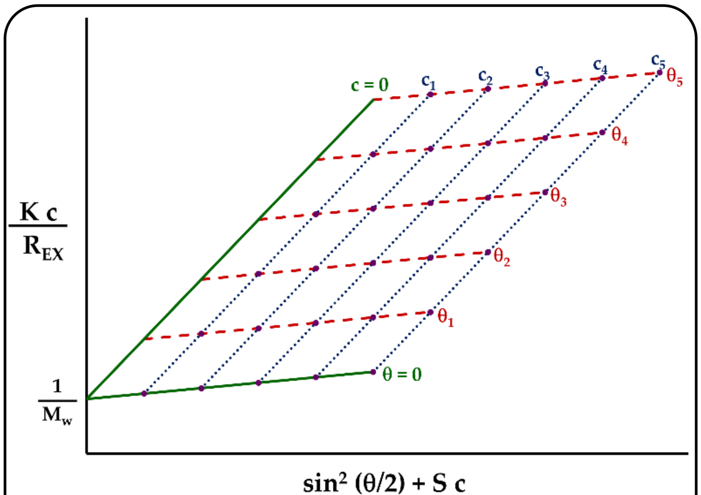

Figure 1. A typical Zimm plot generated from static light scattering measurements at varying angles (θ_i) and varying concentrations (c_i).

A researcher wants to characterize a particular polystyrene sample (dn/dc = 0.11 mL/g) to determine the M_w, R_g, and A_2. After performing SLS measurements at 25°C for a series of solutions of the polystyrene in toluene at varying angles, the researcher observed the data presented in Table 1. If the measurements were performed using a 660 nm laser and the Rayleigh ratio and refractive index for toluene are 1.15×10^{-3}/m and 1.4968, respectively, construct a Zimm plot and analyze it to determine M_w, R_g, and A_2.

Table 1. Measured excess Rayleigh ratios for a series of polystyrene solutions measured at varying angles.

Polystyrene concentration (g/L)	**10^5/cm^{-1} x R_{EX} Measured at θ =**							
	60°	**70°**	**80°**	**90°**	**100°**	**110°**	**120°**	**130°**
5.57	4.001	4.079	4.142	4.052	4.058	4.045	4.025	3.986
4.46	3.998	3.912	3.918	3.900	3.918	3.868	3.852	3.846
3.34	3.489	3.591	3.586	3.532	3.540	3.498	3.487	3.483
2.23	2.911	2.996	2.990	2.941	2.946	2.870	2.854	2.835
1.11	1.819	1.871	1.849	1.811	1.899	1.748	1.732	1.716

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