

Determination of Weight-Average Molecular Weights of Polymers in Chromophoric Solvents Using Low-Angle Laser Light Scattering

The determination of weight-average molecular weights of polymers using low-angle light scattering with a laser light source is a well-established method.¹ Once appropriate instrument constants have been determined, no further calibration is necessary. Nevertheless, this method cannot be used when dealing with colored polymer solutions as found in some biological systems, partially oxidized polymers, polymers with bound chromophoric groups, or macromolecular composites such as lignins, for the absorption of the solvent or/and the polymer will interfere with light scattering measurements. In these cases, the inherent chromophores cannot be removed by normal purification techniques, and the results obtained by straightforward application of the usual method may lead to serious errors. In order to be able to interpret correctly the results obtained using low-angle light scattering methods on colored solutions, a study has been undertaken in which the behavior of known \bar{M}_w polymer solutions has been investigated.

The usual molecular weight determination methodology involves the measurement of the excess Raleigh parameter \bar{R}_θ at various polymer concentrations and using the following equation to determine the weight-average molecular weight \bar{M}_w :

$$\frac{K \cdot c}{\bar{R}_\theta} = \frac{1}{\bar{M}_w} + 2A_2 \cdot C \quad (1)$$

where K is a constant that depends on the nature of the polymer and instrument parameters and A_2 is the second virial coefficient of the solute. The extrapolation of the plot of eq. (1) to zero concentration provides the weight-average molecular weight of the polymer; and the slope, the interaction parameter A_2 .

Two different methods have been used to modify the low-angle laser light scattering method for the determination of \bar{M}_w of polymers in colored solutions. In the first one, excess Raleigh parameters are measured from solutions of polymers which are successively diluted with solvent of the same optical density of the original polymer solution, thus maintaining the absorbance of the sample constant. In the second method, the original polymer solution is diluted with colorless solvent.

All measurements were done on a Chromatix CMX-100 low-angle laser light scattering photometer equipped with a Ne-Ar laser as a light source ($\lambda = 662.8$ nm).

Samples of sodium polystyrenesulfonate standards (Pressure Chemical Co.) of molecular weights 6500, 17,500, 38,000, 70,000, 100,000, 178,000, and 750,000 were used as probes. Methylene blue (C. Erba), with maximum absorbance at 665 nm, was added to regulate the optical density of the solutions. All experiments were performed at room temperature and the ionic strength of the solutions was kept constant at 0.05M with NaNO₃ to avoid metachromic interactions between the dye and the polymer.

The excess Raleigh scattering parameter \bar{R}_θ corresponds to the difference between the light scattered by the polymer solution and that of the pure solvent

$$\bar{R}_\theta = R_\theta(\text{soln}) - R_\theta(\text{solv}) \quad (2)$$

In turn, each of the scattering parameters is determined by the ratio of the intensity of the light scattered by the solution and the incident light

$$\bar{R}_\theta = P/P_0 \quad (3)$$

When the scattering solution is colored, the readings at the photocell will be reduced by a factor corresponding to the absorbance of the solution. Defining $P'(\text{soln})$ and $P'(\text{solv})$ as the readings of the photocell when using colored polymer solutions and colored solvent:

$$P'(\text{soln}) = P(\text{soln}) \times 10^{-A}, \quad P'(\text{solv}) = P(\text{solv}) \times 10^{-A} \quad (4)$$

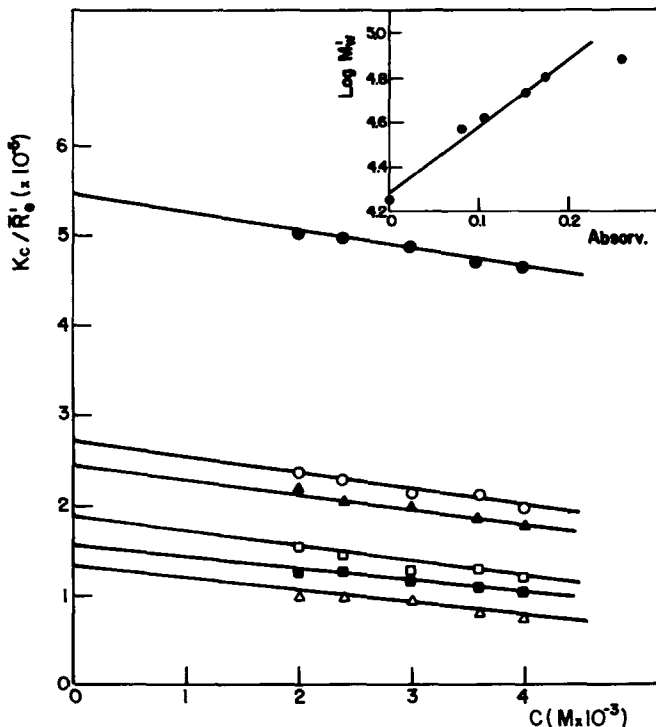


Fig. 1. Molecular weight determination of polystyrenesulfonate ($\bar{M}_w = 17,500$) in colored solutions by the constant absorbance method: (●) $A = 0$; (○) $A = 0.083$; (▲) $A = 0.107$; (□) $A = 0.153$; (■) $A = 0.176$; (△) $A = 0.263$.

where A is the absorbance of the solution in the scattering cell. From eqs. (2)–(4) and defining R' as P'_θ/P_0

$$\bar{R}_\theta = R'_\theta(\text{soln}) \times 10^A - R'_\theta(\text{solv}) \times 10^A$$

$$\bar{R}_\theta = \bar{R}'_\theta \times 10^A \quad (5)$$

where \bar{R}'_θ is a modified excess Raleigh parameter, measured directly on the colored solution. Introducing this factor in eq. (1),

$$\frac{Kc}{\bar{R}'_\theta} = \frac{10^A}{\bar{M}_w} + 2A_2 \cdot c \times 10^A \quad (6)$$

A plot of Kc/\bar{R}'_θ as a function of c will extrapolate linearly to $10^A/\bar{M}_w (= E)$.

Thus, a semilogarithmic plot of $\log E$ vs. absorbance will extrapolate to $\log \bar{M}_w$ at zero absorbance.

This approach has been evaluated for polystyrenesulfonate–methylene blue mixtures in water, with absorbances between 0 and 0.30. An example of the results obtained with polystyrenesulfonate ($\bar{M}_w = 17,500$) is shown in Figure 1, and the insert in that figure shows the graph of $\log E$ vs. A . Results for other molecular weights are shown in Table I.

To determine molecular weights by this method, the solutions should be diluted with a solvent of the same absorbance of the original solution. It has been found that the semilogarithmic relationship is linear up to absorbances of ca. 0.15. Above this value, the absorbance of the solutions is such that insufficient light reaches the photocell, introducing errors in the determinations. This method requires a previous calibration with known molecular weight standards.

TABLE I
Weight-Average Molecular Weight Determinations of Polystyrenesulfonates in Solutions
Containing Methylene Blue, Using the Constant Absorbance
and Variable Absorbance Methods

Standard \bar{M}_w	Constant absorbance method	Variable absorbance method
6500	—	7300 ± 200
17,500	$19,000 \pm 1,000$	—
38,000	$47,000 \pm 3,000$	$43,000 \pm 3,000$
70,000	$78,000 \pm 2,000$	—
100,000	$98,000 \pm 1,000$	$95,000 \pm 4,000$
178,000	$184,000 \pm 1,000$	$175,000 \pm 10,000$
750,000	$804,000 \pm 5,000$	—

An alternative method consists in diluting the initially absorbing solution with pure transparent solvent. By means of the approaches already described, eq. (1) can be transformed to

$$\frac{Kc}{R'_\theta(\text{soln}) \times 10^4 - R'_\theta(\text{solv})} = \frac{1}{\bar{M}_w} + 2A_2 \cdot c \quad (7)$$

In this method $R'_\theta(\text{solv})$ is the scattering parameter for the pure solvent, whereas $R'_\theta(\text{soln})$ has to be recalculated from the experimental value $R'_\theta(\text{soln})$ by multiplying by 10^4 . An example of the experiments performed with polystyrenesulfonate ($\bar{M}_w = 100,000$) solutions with absorbance up to 0.30 is shown in Figure 2, and the results for other molecular weights are listed in Table I.

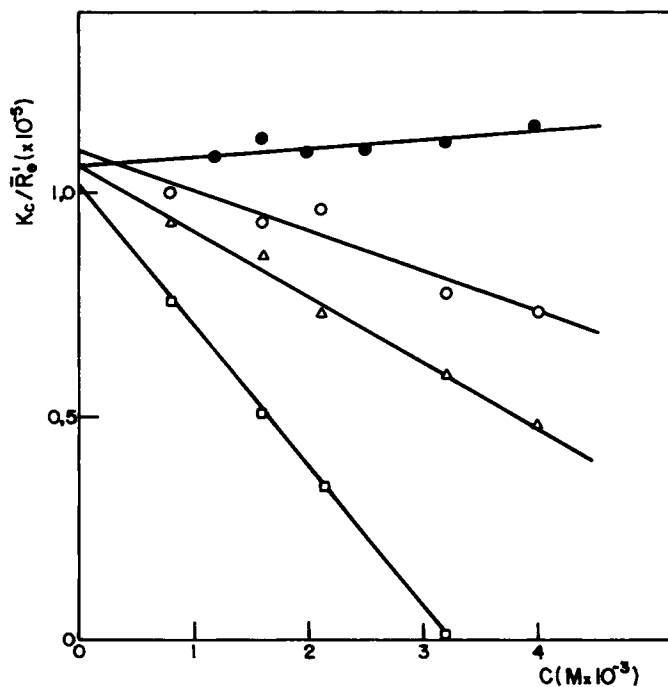


Fig. 2. Molecular weight determination of polystyrenesulfonate ($\bar{M}_w = 100,000$) in colored solutions by the variable absorbance method: (●) $A = 0$; (○) $A = 0.109$; (△) $A = 0.153$; (□) $A = 0.344$.

This procedure does not require any calibration and provides good results even for solutions of high optical density. In both cases, the value for the second virial coefficient A_2 loses its physical meaning as the interactions are not only between the polymer molecules, but also with the chromophoric entities.

Reference

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