One-point Method to Calculate Molecular Weight from Low-Angle Laser Light Scattering Data. I. Application to Acrylamide Polymers

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Synopsis

A new method for the calculation of the weight-average molecular weight from low-angle laser light scattering data has been developed which only requires the measurement of the Rayleigh factor at a single concentration. The method requires the knowledge of the dependence of the second virial coefficient on molecular weight and has been applied to polyacrylamides ranging in molecular weight from 10,000 to 9,000,000. The new method improves the accuracy of light scattering measurements to $\pm 4.7\%$ compared with $\pm 11.2\%$ for the conventional procedure and requires only one-fourth the time. The effect of polydispersity has been included in the procedure. The method is general and is recommended for all linear polymers.

INTRODUCTION

Low-angle laser light scattering photometry is a relatively slow procedure for the determination of weight-average molecular weight. In a typical day of operation it is possible to measure a maximum of three to four samples. Furthermore, the accuracy of the LALLS procedure is limited to about $\pm 10\%$, requiring duplication in order to obtain confident estimates. Therefore, a procedure is needed from which we can improve the accuracy in the estimation of the weight-average molecular weight, so that duplicate measurements are either expedient or unnecessary. This will be done by statistically scrutinizing the conventional LALLS procedure with the aim of isolating and reducing some of the variance that exists in the measurement of molecular weight.

EXPERIMENTAL

Polyacrylamide was synthesized in this laboratory by two methods. The low molecular weight polymer (< 1 million) was synthesized by free-radical aqueous solution polymerization using ethanol mercaptan as a chain transfer agent. High molecular weight polymer was obtained by inverse-microsuspension polymerization using sorbitan monooleate as a stabilizer and Isopar K as the continuous phase. The aqueous phase consisted of monomer solutions, ranging from 30 to 50% by weight, in distilled deionized water. In all

experiments a water-soluble initiator, potassium persulfate, was used. Versenex 80 was used to remove the metal ions from the acrylamide monomer.

Polymerizations were performed at 40, 50, and 60°C, in a 1-gal batch reactor. Further details on the experimental procedure will be discussed in a later paper.

Molecular weights were measured using a Chromatix KMX-6 LALLS photometer, with a cell length of 15 mm and a field stop of 0.2. This corresponded to an average scattering angle of 4.8°.

A 0.45-μm cellulose-acetate-nitrate filter (Millipore) was used for polymer solutions. A 0.22-μm filter of the same type was used to clarify the solvent. Distilled deionized water with 0.02M Na_2SO_4 (analytical grade) was used as a solvent.

The refractive index increment of the solvent was determined using a Chromatix KMX-16 laser differential refractometer at 25°C and a wavelength of 632.8 nm. The dn/dc was found to be 0.1869 mL/g.

The polymer concentrations used in LALLS were determined using a linear calibration between differential refractive index (Δn) and concentration. This calibration was established using a polymer dried at 60°C for 48 h whose concentration was corrected for water content by the Karl Fischer titration procedure.

All polymers were unfractionated with polydispersities between 2.0 and 2.5, as determined by aqueous size exclusion chromatography.

The acrylamide polymers were analyzed for possible acrylic acid groups by ^{13}C-NMR, infrared spectroscopy, elemental analysis, and titration.[1] In all measurements no hydrolysis was detected, and this confirmed that the polymer was indeed a homopolymer of acrylamide.

THEORY

Light Scattering

The scattering of light in liquid media was first discussed by Lord Rayleigh in 1871[2] and over the years has been given the name of Rayleigh scattering. This is described by the Rayleigh factor, R_θ, defined as

$$R_\theta = J_\theta/(I_0 V)$$

where J_θ is the radiant intensity (W/s) at a scattering angle θ. I_0 is the irradiance of the illuminating beam (W/cm^2) and V is the scattering volume.

Debye was the first to apply Rayleigh scattering to polymers.[3-5] He showed that light scattering could be used to determine the molecular weight and also the second virial coefficient; a characteristic of the solute–solute interactions. In 1948, Zimm[6] introduced the well-known double extrapolation procedure to zero concentration and zero scattering angle. With the advent of laser light scattering photometers,[7] the scattering could be viewed at low angles, only a few degrees off the path of the incident beam. This eliminated the need for angular extrapolation.

When low-angle laser light scattering is used, the Rayleigh factor can be calculated from

$$R_\theta = \frac{G_\theta}{G_0}\left(\frac{D}{\sigma'l'}\right)$$ (1)

where G_θ and G_0 are the photomultiplier signals for the scattered and incident beams. D is the transmittance of the attenuators used in measuring G_0, σ' is the solid angle over which the scattered light is viewed, and l' is the length of the scattering volume parallel to the incident beam.

For optically isotropic polymers the relationship between the Rayleigh factor and the weight-average molecular weight is given by

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w P_\theta} + 2A_2c + 3A_3c^2 + \cdots$$ (2)

where K is an optical constant defined as

$$K = \left(\frac{2n^2n^2}{\lambda^4 N_a}\right)\left(\frac{dn}{dc}\right)^2$$

where n is the refractive index of the solvent at the incident wavelength λ, N_a is Avogadro's number, and dn/dc is the specific refractive index increment. R_θ is the excess Rayleigh factor of the solution over the solvent defined as

$$R_\theta = R_{\theta_{\text{SOLUTION}}} - R_{\theta_{\text{SOLVENT}}}$$

where $\overline{M}_w$ is the weight-average molecular weight, A_2 and A_3 are the second and third virial coefficients, and $P(\theta)$ is the particle scattering function.

For particles larger than $\lambda/20$, scattered light coming from different parts of the same particle will interfere and cause a reduction in the intensity of the scattered light by a factor $P(\theta)$ represented by

$$P(\theta) = 1 + \frac{16n^2}{3\lambda^2}\langle S^2\rangle\sin\left(\frac{\theta}{2}\right)$$

where $\langle S^2\rangle$ is the mean square radius of gyration. At low scattering angles $P(\theta) \simeq 1$.

For dilute polymer solutions the quadratic and higher order terms in the virial expansion are negligible, and eq. (2) reduces to

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + 2A_2c$$ (3)

This equation is strictly valid only at $\theta = 0$, but is a very good approximation at low scattering angles.

TABLE I
Values of the Parameters α and β in the Expression $A_2 = \alpha\overline{M}_w^\beta$ for Several
Polymer–Solvent Systems

Polymer–solvent combination	$\alpha \times 10^3$	β	References
Polyacrylamide in $0.02M$ Na_2SO_4	8.18	-0.211	This work
Poly(ethylene oxide) in methanol	37.9	-0.320	This work
Poly(methyl methacrylate) in THF	6.62	-0.242	This work
Poly(methyl methacrylate) in acetone	3.51	-0.221	This work
Poly(methyl methacrylate) in dioxan	—	-0.32	This work
Poly(methyl methacrylate) in butyl acetate	—	-0.34	This work
Polystyrene–toluene	12.41	-0.269	This work
Polystyrene–toluene	—	-0.22	Casassa and Markowitz[9]
Polystyrene–butanone	2.73	-0.247	This work
Polystyrene–butanone	—	-0.264	Ishihara and Koyama[8]
Polystyrene–dichloroethane	—	-0.296	Ishihara and Koyama[8]

Second Virial Coefficient

The second virial coefficient accounts for the interaction of two polymer chains that are in close contact with each other. These can be divided into two categories. Intermolecular interactions occur between segments of two polymer chains and intramolecular interactions are caused by Van der Waals
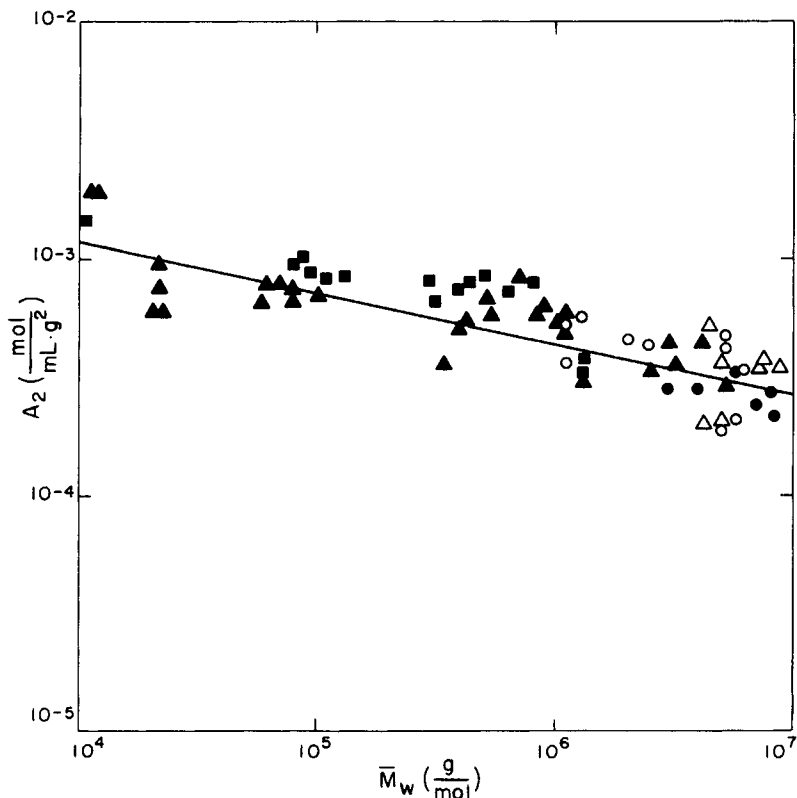

Fig. 1. Relationship between the second virial coefficient and molecular weight for polyacrylamide in $0.02M$ Na_2SO_4: (▲) this work; (■) Stanislawczyk[25]; (△) Kulicke et al.[26]; (●) Kim[27]; (○) Klein and Conrad.[28]
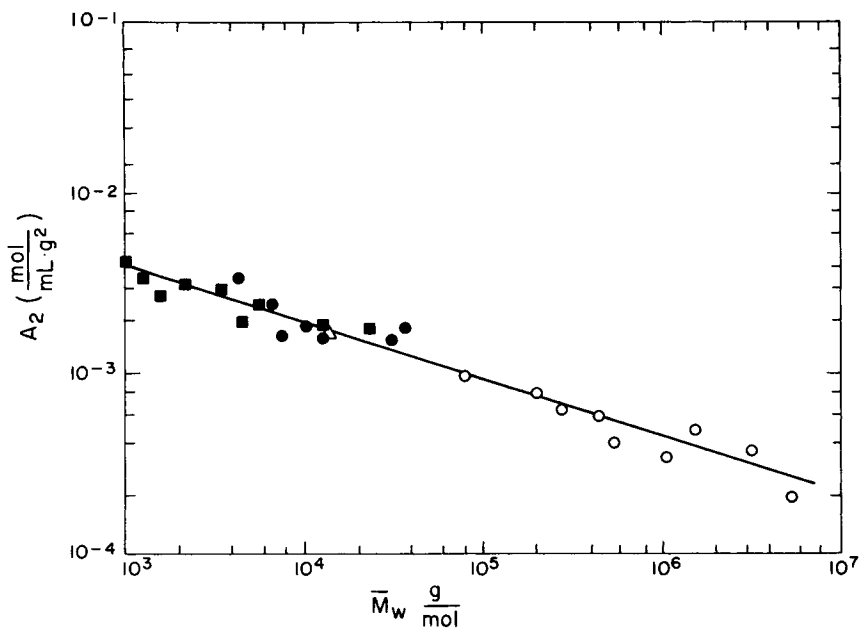
Fig. 2.   Relationship between the second virial coefficient and molecular weight for polyethyleneoxide in methanol: (●) Elias and Lys[29]; (○) Allen et al.[30]; (△) Moldovan and Strazielle[31]; (■) Ritscher and Elias.[32]
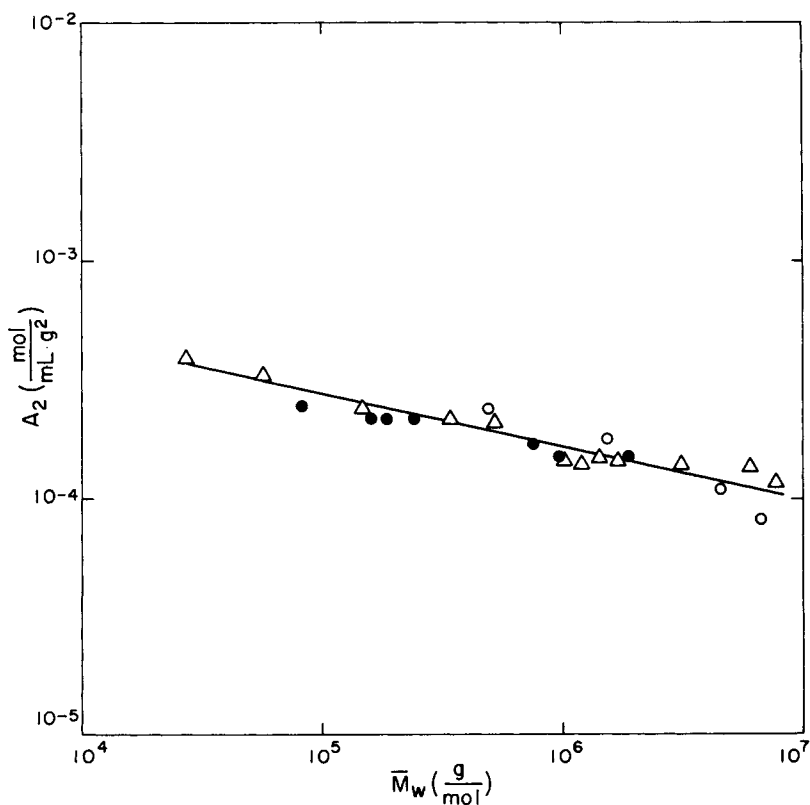

Fig. 3.   Relationship between the second virial coefficient and molecular weight for polymethylmethacrylate in acetone: (●) Bishoff and Desreux[33]; (○) Schulz and Craubner[34]; (△) Cantow and Schulz.[35]
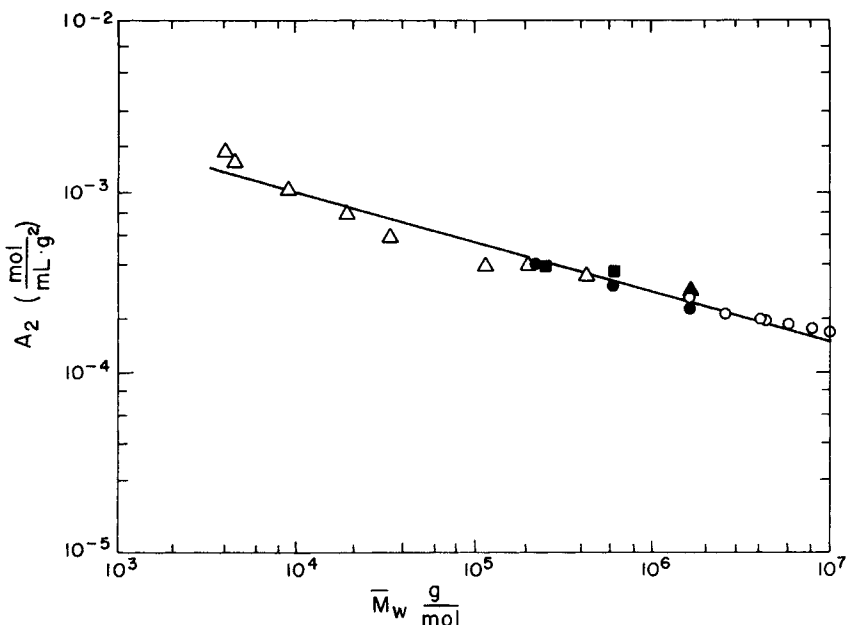
Fig. 4. Relationship between the second virial coefficient and molecular weight for polystyrene in toluene: (●) Schulz et al.[36]; (▲) Outer et al.[37]; (■) Schulz and Hellfritz[38]; (○) Fukada et al.[39]; (△) Zhang et al.[40]

forces between nonbonded segments of the same molecule. These are also referred to as excluded volume effects.

High values of the second virial coefficient (A_2) indicate strong polymer–polymer interactions, and at the theta temperature, or in a theta solvent, A_2 vanishes.

The second virial coefficient is experimentally observable through osmotic pressure or light scattering studies. Several investigators[8-11] have found that A_2 depends on the molecular weight of the polymer. The relationship is usually expressed by the following empirical form for linear polymers:

$$A_2 = \alpha M^\beta \tag{4}$$

where α and β are constants independent of the molecular weight and M is the molecular weight of the polymer which is assumed to be monodisperse. Table I gives values of α and β for several polymer–solvent combinations.

Figures 1–4 show this relationship for polyacrylamide, polystyrene, poly(methyl methacrylate) and poly(ethylene oxide). The linear dependence between A_2 and M_w on a log–log scale is verified for a variety of polymer compositions in several solvents, indicating the universality of the relationship between the second virial coefficient and molecular weight for linear polymers. However, the scattering in these plots indicates that the accuracy in experimentally determining A_2 is poor. This is particularly true for polyacrylamide because of the larger errors involved in LALLS measurements in aqueous solutions.[12]

These inaccuracies in the measurement of the second virial coefficient lead to large errors in the estimates of molecular weights. In Figure 5 the fluctua-
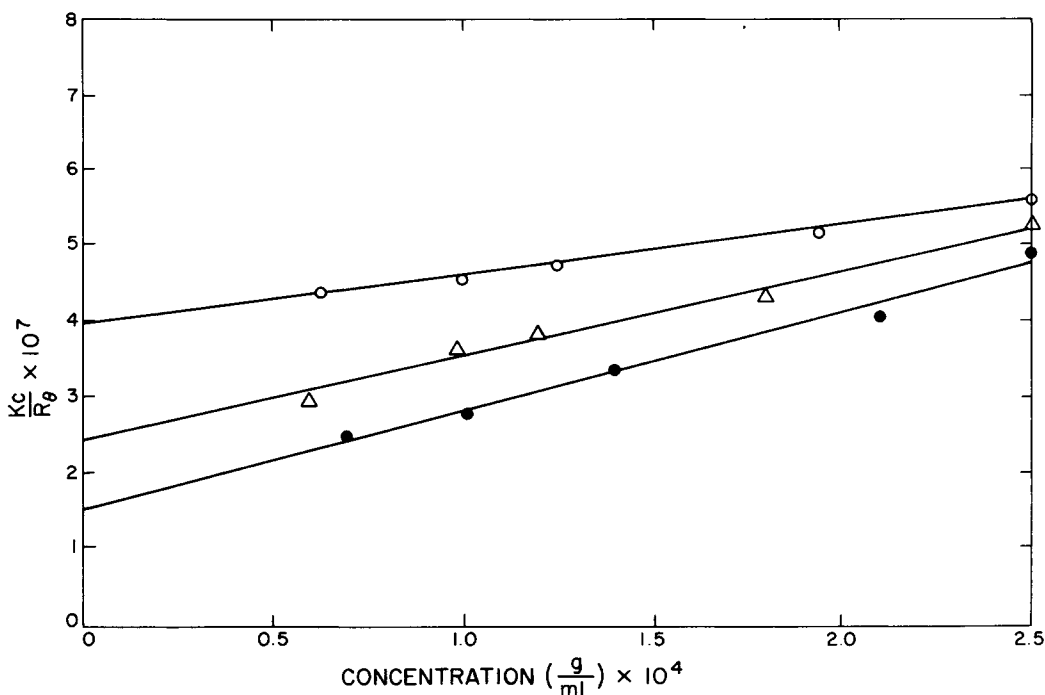
Fig. 5. Kc/R_θ vs. concentration for a high molecular weight sample of polyacrylamide measured on three occasions.

tion in the calculated molecular weights of a polymer measured on three occasions is seen to be almost exclusively caused by variations in the slope. Therefore, to improve the accuracy of LALLS a new method is needed from which estimates of the weight-average molecular weight can be obtained without relying on the experimental determination of the second virial coefficient.

Relationship of β to the Mark–Houwink–Sakurada Exponent

Flory and Orifino[13] have shown that for high molecular weight polymers in good solvents the second virial coefficient can be expressed as

$$\frac{A_2 M}{[\eta]} = \text{const}^* \tag{5}$$

where M is the molecular weight and $[\eta]$ is the intrinsic viscosity, given by

$$[\eta] = KM^a \tag{6}$$

Combining eqs. (5) and (6) yields after rearrangement:

$$A_2 = C_1 M^{a-1} \tag{7}$$

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*Flory and Orifino found this dimensionless constant to be 150, but other authors[13-16] have found values ranging from 110 to 160, where $[\eta]$ has the units dL/g.
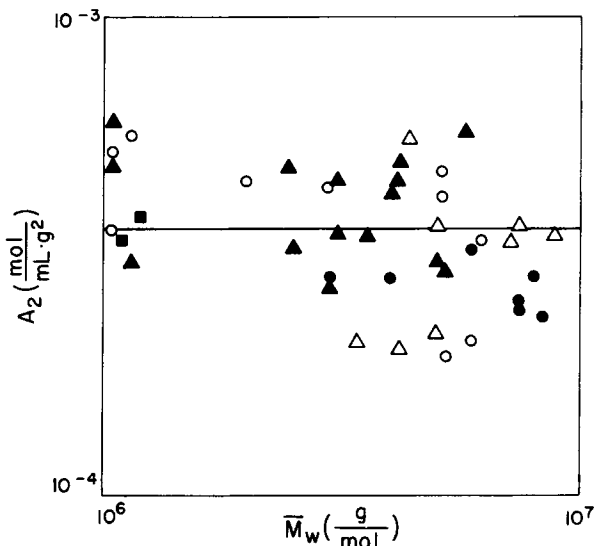
Fig. 6. Relationship between the second virial coefficient and molecular weight for high molecular weight polyacrylamides in $0.02 M$ Na_2SO_4. Symbols are the same as in Figure 1.

Equation (7) suggests that the second virial coefficient is dependent on the molecular weight, and this dependence is related to the exponential term of the Mark–Houwink–Sakurada equation ($\beta = a - 1$). Hence, from viscosity data we have an *a priori* estimate of the strength of the relationship between the second virial coefficient and molecular weight.

For a poor solvent, $a = 0.5$ and $A_2 = C_1 M^{-0.5}$. For very good solvents $a \to 1$ and $A_2 = C_1$, independent of molecular weight. Therefore, as the solvent power rises, the influence of molecular weight on the second virial coefficient is reduced, and, in extremely good solvents, the second virial coefficient is independent of molecular weight. This has been verified experimentally by several investigators[17-20] and is shown for polyacrylamide of very high molecular weights in Figure 6.

For polyacrylamide, the Mark–Houwink–Sakurada equation at 25°C in water is[12]

$$[\eta] = 5.6 \times 10^3 M^{0.8}$$

This suggests $\beta = -0.2$, which agrees with the experimental value of -0.211, determined later herein.

Table II summarizes the values of a and β for various polymer–solvent systems.

Effect of Polydisperity on the Second Virial Coefficient

We have shown in eq. (4) that, for a monodisperse polymer, with molecular weight M, the second virial coefficient is given by

$$A_2 = \alpha M^\beta$$

TABLE II
Relationship between the Mark–Houwink–Sakurada Exponent a and the Exponent β
in the Equation $A_2 = \alpha \overline{M}_w^\beta$

Polymer–solvent combination	Temperature (°C)	a	$a - 1$	β
Polyacrylamide in 0.02M Na$_2$So$_4$	25	0.80	-0.20	-0.211
Polystyrene–toluene	25	0.79	-0.21	-0.22
Polystyrene–butanone	25	$0.58 \to 0.635$	$-0.365 \to -0.42$	$-0.264, -0.247$
Polystyrene in dichloroethane	25	$0.66 \to 0.74$	$-0.26 \to -0.34$	-0.296
Poly(ethylene oxide) in methanol	25	0.72	-0.28	-0.320
Poly(methyl methacrylate) in acetone	25	$0.69 \to 0.73$	$-0.27 \to -0.31$	-0.221

where α and β are characteristics of the polymer–solvent pair at a given temperature and are independent of molecular weight.

For polydisperse molecular weights, the average second virial coefficient (A_2) can be expressed as

$$\overline{A}_2 = \frac{\int_0^\infty \int_0^\infty A_2(m, n) m f(m) n f(n) \, dm \, dn}{\int_0^\infty \int_0^\infty m f(m) n f(n) \, dm \, dn} \tag{8}$$

where $A_2(m, n)$ is the interaction between two polymer chains of length m and n:

$$A_2(m, n) mn = \frac{\alpha}{8} \left[m^{(2+\beta)/3} + n^{(2+\beta)/3} \right]^3 \tag{9}$$

Other forms of $A_2(m, n)$ are possible,[†] but eq. (9) is preferred because it assumes the interactions between chain elements are similar to those between two hard spheres. This is a basic assumption of excluded volume treatments of dilute polymer solutions,[13] where a molecule is represented as an impenetrable sphere with a volume proportional to the cube of the radius of gyration.

Now, we adopt the approach of Casassa[22] and assume the molecular weight distribution is adequately described by the Schulz distribution:

$$f(m) = \frac{y^{z+1} m^z e^{-ym}}{\Gamma(z + 1)}$$

$$y = \frac{z + 1}{\overline{M}_w} \tag{10}$$

where $f(m) \, dm$ is the weight fraction of solute with molecular weight m and

[†] Other authors[21] have expressed $A_2(m, n)$ as the simple geometric mean of virial coefficients of monodisperse polymers of length m and n, respectively.

$\Gamma(z)$ is the gamma function. The parameter z corresponds to the polydispersity, where $z = \infty$ is a monodisperse sample and $z = 1$ corresponds to the most probable distribution and a polydispersity of 2.

Equations (9) and (10) are inserted into eq. (8) and integrated to yield

$$\overline{A}_2 = \phi A_{2,ww} \tag{11}$$

where $A_{2,ww}$ is the second virial coefficient of a monodisperse polymer with a molecular weight equal to $\overline{M}_w$ of the polydisperse sample, and is given by

$$A_{2,ww} = \alpha \overline{M}_w^\beta \tag{12}$$

ϕ is a constant which is dependent on the polydispersity and the parameter β, and is given by

$$\phi = \frac{(z+1)^{-\beta}}{4[\Gamma(z+2)]^2} \cdot \left\{ \Gamma(z+3+\beta)\Gamma(z+1) \right.$$
$$\left. + 3\Gamma\left[\frac{(3z+17+2\beta)}{3}\right]\Gamma\left[\frac{(3z+5+\beta)}{3}\right] \right\} \tag{13}$$

Combining eqs. (11) and (12)

$$\overline{A}_2 = \phi\left(\alpha \overline{M}_w^\beta\right) \tag{14}$$

Equation (14) shows that β, the dependence of the second virial coefficient on molecular weight, is independent of the polydispersity and that the second virial coefficients of polymers with different polydispersities can be compared provided they are corrected by a factor ϕ. The effect of polydispersity on the value of ϕ is shown in Table III.

For polyacrylamide, with a molecular weight distribution taken as the most probable, eq. (14) reduces to

$$\overline{A}_2 = 1.07\alpha \overline{M}_w^\beta \tag{15}$$

In other words, the second virial coefficient of a polyacrylamide with a

TABLE III
Effect of the Polydispersity on the Second Virial Coefficient for Polyacrylamide

Polydispersity	ϕ (with $\beta = -0.211$)
1.0	1.0
1.2	1.028
1.5	1.054
2.0	1.071
2.5	1.094
3.0	1.104
5.0	1.123
100.0	1.149

polydispersity of 2.0 is 7% larger than the second virial coefficient that would occur if the polymer were monodisperse with a molecular weight equal to $\bar{M}_w$ of the polydisperse sample.

All second virial coefficients measured in this study were corrected for polydispersity using the above procedure.

Modeling the Second Virial Coefficient

Many theories exist for modeling the second virial coefficient and its dependence on molecular weight. The Kurata–Yamakawa–Tanaka theory is generally accepted as the best in predicting second virial coefficients from measurements of molecular weight and the mean-square radius of gyration. However, Kok and Rudin[23] have developed a method to predict A_2 from intrinsic viscosities, and it appears to be marginally better than the K–Y–T theory for the polymers studied. A complete discussion of this topic is given by Yamakawa.[24]

RESULTS AND DISCUSSION

New One-Point LALLS Method

In conventional low-angle laser light scattering a series of polymers are prepared at different concentrations and the Rayleigh factor is measured. A plot of Kc/R_θ vs. c is constructed, and the weight-average molecular weight is obtained by linear extrapolation to zero concentration; the slope of the line is twice the second virial coefficient. This procedure, although statistically
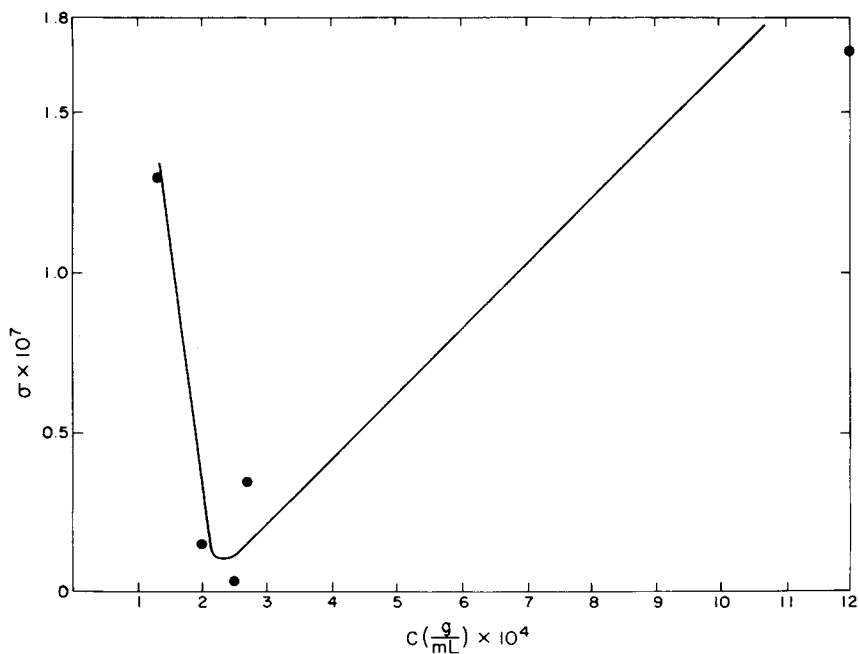

Fig. 7. Standard deviation of Kc/R_θ as a function of concentration for a polyacrylamide measured on several occasions.
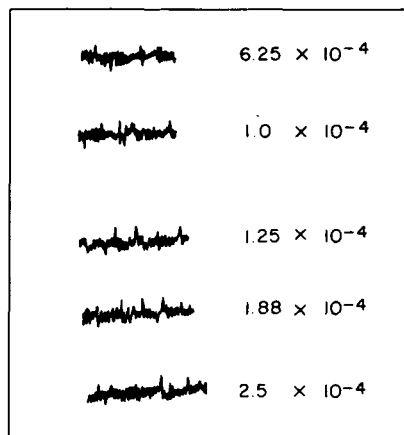
Fig. 8. Variation in the photomultiplier signal of the scattered light (G_θ) for several concentrations (g/mL).

poor because concentration appears on both axis, is nonetheless valid provided the variance of all the measurements is the same. However, as Figure 7 shows, the variance is indeed not constant and passes through a minima as a function of concentration. This is the result of two effects:

1. At very low concentrations the photomultiplier signal and the Rayleigh factor are small. The variation in this signal with time is, however, a constant which is independent of concentration (Fig. 8). Therefore the instrument is less sensitive at low concentrations due to a lower signal-to-noise ratio. This
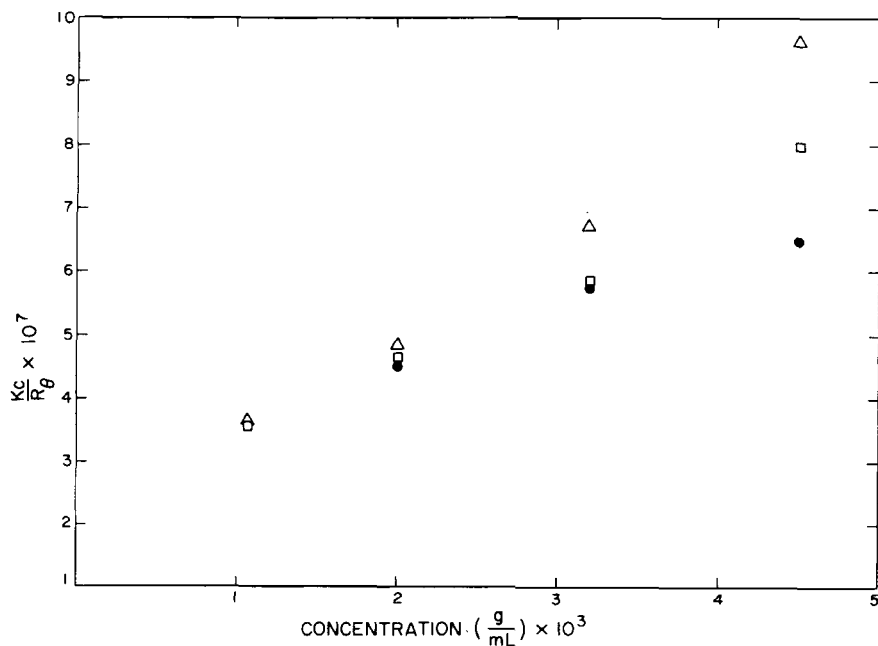

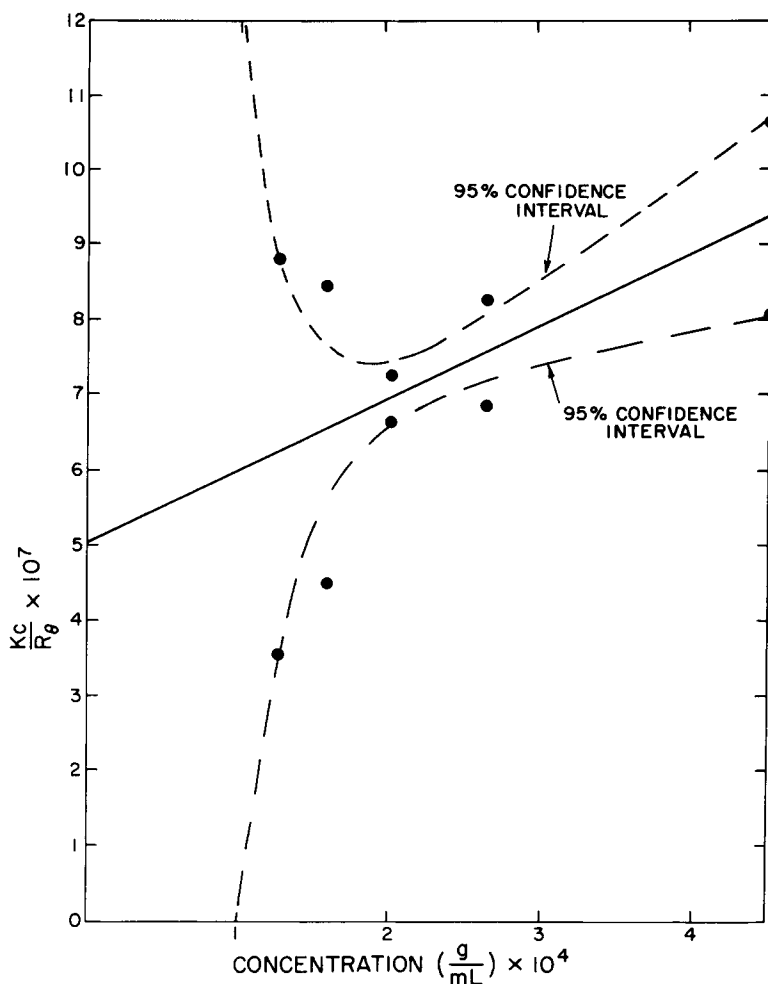Fig. 9. Kc/R_θ vs. concentration for a polyacrylamide sample measured on three occasions.

Fig. 10. Ninety-five percent confident intervals of Kc/R_θ as a function of concentration.

leads to irreproducible estimates of molecular weight when measured at low concentrations, as is shown in Figure 5.

2. At high concentrations the filtering of the polymer, before it enters the light scattering cell, is difficult, due to polymer retention on the membrane. This problem can only be circumvented by using a larger pore-size filter. This however, introduces impurities into the cell which causes large variations in the photomultiplier signal. The baseline often becomes obscured, and the measurement is unreliable. An example of this phenomena is observed in Figure 9.

Figure 10 shows the experimentally determined 95% confidence region for a polyacrylamide sample. The degree of uncertainty is largest at low concentrations, which is the very region we are extrapolating to in order to obtain the molecular weight. These large variances in Kc/R_θ lead to poor estimates of the slope and the second virial coefficient. These inaccuracies are translated

into a poor estimate of molecular weight when extrapolating to zero concentration.

To improve the estimate of molecular weight, we could perform weighted least-squares analysis, where each value of Kc/R_θ is weighted by the reciprocal of its variance, However, this procedure would require several measurements of Kc/R_θ at each concentration, and from a practical point of view this is not feasible.

The weighted least-squares procedure can be simplified by setting the weighting of all points to zero except the one for which we have the most confidence. That is, we measure only at a single concentration at which the variance in Kc/R_θ is smallest. If we take the example shown in Figure 6, this would be at a concentration of 2×10^{-4} g/mL. The molecular weight is then obtained by extrapolating to zero concentration using values of A_2 from previous light scattering measurements, such as in Figures 1–4. This gives us
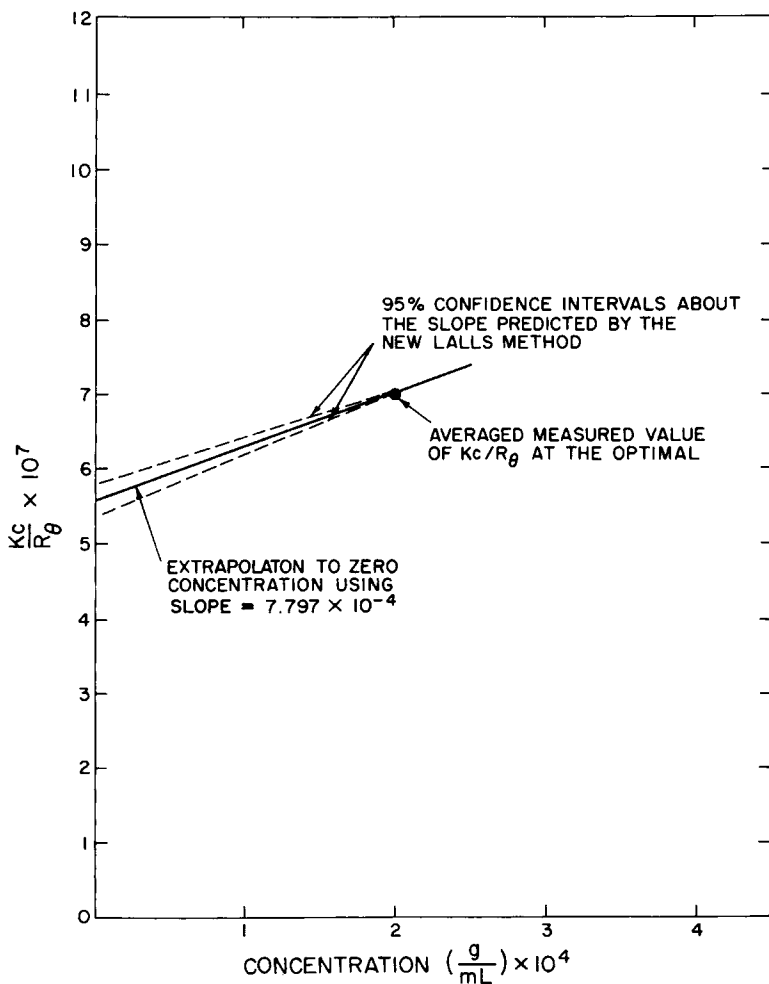

Fig. 11. Confidence region for weight average molecular weight predicted from the new LALLS procedure.

more confidence in the estimate of weight-average molecular weight than if we calculated the slope from a few dilutions. Figure 11 shows that by using a historical value of A_2 the confidence interval of the estimate of the weight average molecular weight is reduced significantly over the conventional procedure.

Method of Calculation for the New LALLS Procedure

We recall that the molecular weight is related to the Rayleigh factor by

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + 2A_2 c \tag{3}$$

where

$$A_2 = \alpha M^\beta \tag{16}$$

Combining eqs. (3) and (16), we obtain

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_w} + 2\alpha \overline{M}_w^\beta c \tag{17}$$

For polyacrylamide, these parameters and the 95% confidence intervals are

$$\alpha = 0.00818 \pm 0.00380$$

$$\beta = -0.211 \pm 0.037$$

Substituting these values into eq. (17) yields

$$\left(\frac{Kc}{R_\theta}\right)_0 = \frac{1}{\overline{M}_w} + \left(1.636 \times 10^{-2}\overline{M}_w^{-0.211}\right)C_0 \tag{18}$$

From eq. (18) we can predict the weight-average molecular weight from a single measurement at a concentration (C_0) where the variance is smallest, $(K_c/R_\theta)_0$. These concentrations have been determined for polyacrylamide and are listed in Table IV. These represent optimal values for measurement in the sense that they produce the lowest confidence intervals in the estimate of weight-average molecular weight. Table V shows the molecular weights predicted by the conventional method and by eq. (18). The new method gives a reproducibility of $\pm 4.7\%$ which is less than half the error of the conventional procedure ($\pm 11.2\%$).

This one-point method can be applied to any linear polymer for which the relationship between the second virial coefficient and molecular weight is known or can be elucidated from the literature.[‡] For polymers other than

[‡]For branched polymers, the procedure cannot be used since A_2 does not vary linearly on a log–log scale with the weight average molecular molecular weight. Therefore, eq. (4) is invalid for nonlinear polymers.

TABLE IV
Optimal Concentration for the Measurement of Weight Average Molecular Weight
of Polyacrylamide by LALLS

$\overline{M}_w$ ($\times 10^3$)	Optimal concentration (g/mL)
10 → 30	4×10^{-3}
30 → 70	2.5×10^{-3}
70 → 400	1.5×10^{-3}
400 → 650	9×10^{-4}
650 → 1,000	4×10^{-4}
> 1,000	2×10^{-4}

TABLE V
A Comparison of the Accuracy in the Prediction of Weight Average Molecular Weight
by the Conventional and the New LALLS Procedure

$\overline{M}_w$ (conventional method)	Average deviation (%)	$\overline{M}_w$ (new method)	Average deviation (%)
11,200		11,400	
11,500	1.3	11,200	0.9
21,300		23,200	
21,900		23,500	
22,600	2.0	22,800	1.1
57,000		60,900	
61,500		63,000	
72,500	9.3	73,700	7.9
79,000		84,000	
80,000		82,000	
81,000	0.8	78,400	2.5
253,000		284,000	
290,000	9.8	248,000	6.8
344,000		422,000	
393,000		407,000	
420,000		405,000	
698,000	25.3	414,000	0.9
576,000		495,000	
617,000		512,000	
800,000	13.6	470,000	3.0
540,000		519,000	
754,000		672,000	
865,000		665,000	
890,000	15.1	640,000	8.4
1,062,000		990,000	
1,136,000		944,000	
1,145,000	3.1	900,000	3.2
1,500,000		1,500,000	
2,400,000		1,600,000	
2,900,000	22.5	2,000,000	11.8
Overall Average deviation	11.2%		4.7%

acrylamide, the parameters in eq. (17) will be different, but the computational procedure remains unchanged.

In a future paper this method will be applied to other polymers including polystyrene and polymethylmethacrylate.

CONCLUSIONS

A method has been developed from which the weight-average molecular weight can be predicted from a measurement of the Rayleigh factor at a single concentration. This method has been found to give a more accurate and reproducible value of M_w in a fraction of the time required for conventional low-angle laser light scattering. The method has been applied to polyacrylamide as an example, but is general and can be applied to any linear polymer provided that the relationship between the second virial coefficient is known or can be determined from experimental data. It is particularly useful for aqueous light scattering.

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