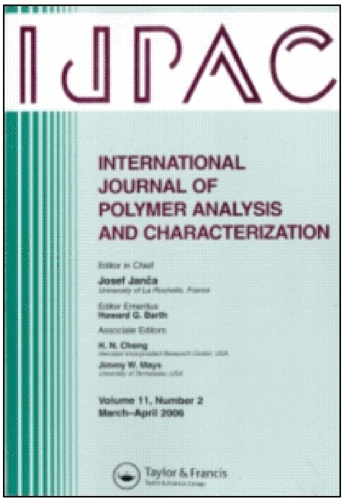

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Improved Precision in Multi-Angle Laser Light Scattering Data Processing

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A general method for improving the precision in the estimation of the root-mean-square radius of linear polymer chains in solution from light scattering data has been developed. Specifically, the variance in the estimation of the Rayleigh factors has been found to depend on the concentration of the measured polymer solution. Therefore, with angle-dependent measurement of the Rayleigh factors, at only a single concentration, the root-mean-square radius can be estimated more precisely (3.7%) than if all the concentrations are employed (7.2%), without sacrificing accuracy. With the knowledge of the dependence of the second virial coefficient on molar mass, the root-mean-square radius can be iterated from the Rayleigh factors of the polymer solution with the lowest variance. This has been applied to aqueous polyacrylamide solutions as well as polystyrene in toluene and 2-butanone; the one-concentration method has been found to improve the precision twofold over classical Zimm data treatments. At the same time the measurement time is shortened significantly. It has also been found that the concentration with the lowest variance depends on molar mass of the polymer and an equation to predict this concentration in general for any polymer-solvent combination has been developed.

Keywords: Static light scattering; Second virial coefficient; Radius of gyration; Polyacrylamide; Polystyrene; Excess Rayleigh ratio

INTRODUCTION

The intensity of light scattered by a system of independent particles is, at a given mass concentration, proportional to their molar mass.

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Debye was the first to apply this to the characterization of polymers[1,2] to estimate weight-average molar mass and an important size parameter of particles in solution, the z-averaged root-mean-square radius. The following brief derivation is necessary for the theoretical and statistical development which ensue and constitute the present contributions. With the approximations of very dilute solutions and only a single interaction with another polymer chain Zimm[3,4] improved light scattering data processing. For optically isotropic polymers, the relationship between the Rayleigh factor and the weight-average molar mass can be expressed in a power series

$$\frac{K^* c}{R_\theta} = \frac{1}{M_\mathrm{w} P_\theta} + 2A_2 c + 3A_3 c^2 + \cdots, \tag{1}$$

where R_θ is the excess Rayleigh ratio, c the mass concentration, P_θ the internal scattering function, A_2 and A_3 the second and third virial coefficients, and M_w the weight-average molar mass. The optical constant K^* contains the refractive index of the solvent, the applied wavelength, Avogadro's number and the specific refractive index increment. For dilute polymer solutions the quadratic and higher order terms in the virial expansion are negligible. A double extrapolation to $\theta = 0$ and $c = 0$ yield Equation (2) from which the weight-average molar mass can be determined.

$$\left(\frac{K^* c}{R_\theta}\right)_{\theta=0, c=0} = \frac{1}{M_\mathrm{w}}. \tag{2}$$

This technique, developed in 1948, is still applied for the determination of molar mass and root-mean-square radius of gyration of polymers which are soluble in organic[5-7] and aqueous solvents.[8] However, Equation (2) requires measurements at various concentrations with a subsequent extrapolation of $c = 0$ to estimate molar mass. Within this extrapolation values of low precision are included with highly precise data, since the variances of different concentrations are not identical, and can differ by two orders of magnitude.[9] This renders the whole estimation less precise with typical deviations of approximately 10% in molar mass and radius of gyration obtained. Some authors report attempts to improve the precision in the estimation in molar mass by modifying the calculations,[10,11] altering the graphical treatment,[12] combining low-angle laser light scattering with sedimentation techniques,[13] or by applying a one-point method.[9,14,15] All these articles have been focused on the determination of the molar mass. The purpose of the present work has been to extend the one-point method[9,14,15] to the estimation of the root-mean-square radius of gyration.

The measurements, which are compared with those from the classical Zimm-technique, have been conducted with polystyrene (PS) and polyacrylamide (PAM) of various molar masses. The dimensions of PAM in aqueous media are very important since these polymers are often used, in solution, for water treatment applications[16–18] and its molar mass range test the applicability of any novel method. Polystyrene has been chosen since this polymer has been the subject of many investigations over the past fifty years[4,10,19–21] and can, to a large extent, be viewed as a model organically soluble macromolecule.

One-Point Method for M_w Estimation

Hunkeler *et al.*[9,14] showed that the weight-average molar mass can be estimated more precisely with the measurement of the excess Rayleigh ratios at a single concentration than with a dilution series. They conducted their measurements with a low angle laser light scattering apparatus (LALLS) at a measuring angle of 4°. For such a small angle, R_θ can be approximated by $R_{\theta=0}$. The dependence of the second virial coefficient on molar mass can be expressed by Equation (3), with only a negligible correction required for polydispersity effects[9] if the most probable distribution is considered

$$A_2 = \alpha M^\beta. \tag{3}$$

The second virial coefficient in Equation (1) can now be replaced by expression (3) to yield

$$\left(\frac{K^*c}{R_\theta}\right)_{\theta=0} = \frac{1}{M_w} + 2c\alpha M_w^\beta. \tag{4}$$

Equation (4) has been written in the limit of $\theta = 0$. The constants α and β in Equations (3) and (4) are characteristics of the polymer-solvent pair and are molar mass independent. From the dependence of A_2 on molar mass of precursory measurements α can be determined, whereas β can be derived from the Mark–Houwink–Kuhn–Sakurada exponent.[22] Equation (4) can therefore be solved by iteration. Once the constants α and β are known only the excess Rayleigh ratio of a single concentration must be considered to estimate weight-average molar mass. It has also been found that the variance changes with concentration and the optimum concentration (OC) is identified to be that where the variance of K^*c/R_θ is the smallest. The values of molar mass obtained with this method at the optimum concentration, revealed an improved precision by a factor of two, relative to the conventional procedure. Additionally, the one-point method required much less time, sample and solvent, since measurements at only one concentration were necessary.

z-Average Mean Square Radius

Due to possible interference of scattered light, a diminution of scattered intensity is observed. The reduction is angle dependent, with P_θ in Equation (5) describing the angular dependence of the scattering intensity with respect to an internal interference.[2] "Internal" refers to interference due to scattering by the same molecule. In the limit as θ approaches 0, P_θ approaches unity, since the scattered intensity is not weakened by interference. At viewing angles larger than zero, the scattering intensity is reduced, with the extent of diminution increasing with increasing θ. The function of P_θ can be expressed as

$$P_\theta = 1 - \frac{16\pi^2 n_0^2}{3\lambda_0^2}\langle r^2\rangle_z \sin^2(\theta/2), \tag{5}$$

where n_0, λ_0, and $\langle r^2\rangle_z$ being the solvent refractive index, the incident wavelength, and the *z*-average size, which is the integral of the mass elements of the molecules weighted by the square of their distances from the molecule center of gravity. The parameter $\langle r\rangle_z$ is referred to as the root-mean-square *z*-average (RMS) radius of gyration. Its estimation is possible with the measurement of the excess Rayleigh ratio at various angles. Equation (5) is valid in general, without any assumption regarding the shape of the macromolecular particle, as long as the second term is much smaller than unity.[2]

At the limit as $\sin^2(\theta/2) \to 0$, the slope m of angle-dependent measurements in a plot of K^*c/R_θ versus $\sin^2(\theta/2)$ is defined by Equation (6) with $k = 2\pi n_0/\lambda_0$.

$$m = \frac{d(K^*c/R_\theta)}{d[\sin^2(\theta/2)]} = \frac{1}{M_\mathrm{w}}\frac{4k^2}{3}\langle r^2\rangle_z. \tag{6}$$

Rearranging of Equation (6) provides an expression of M_w

$$M_\mathrm{w} = \frac{4k^2\langle r^2\rangle_z}{3m} \tag{7}$$

which can be substituted in Equation (4) to yield

$$\left(\frac{K^*c}{R_\theta}\right)_{\theta=0} = \left(\frac{4k^2\langle r^2\rangle_z}{3m}\right)^{-1} + 2c\alpha\left(\frac{4k^2\langle r^2\rangle_z}{3m}\right)^{\beta}. \tag{8}$$

As the left side of this equation is obtained from measured data by extrapolating to $\theta = 0$, the mean square radius can be iterated from Equation (8) in the same way as the weight-average molar mass from Equation (4). Therefore, Equation (8) is the expression which can be used to improve the precision of $\langle r\rangle_z$ estimation, as will be demonstrated herein. This equation is not restricted to the slope m of the data which have been previously obtained by an extrapolation to $c = 0$ of the measured points. In principle any concentration can be used. The transformation of the one-point method to the estimation of RMS radii of gyration results in a procedure where the scattering signals at various angles have to be measured at only one unique concentration with a subsequent extrapolation to $\theta = 0$. At vanishingly small concentrations, Equation (8) reduces to Equation (2). The term "one-point method" would, however, be misleading in this case since several points, at least two, must be measured. Therefore, this term will be replaced for RMS radius estimation by the term "one-concentration method" (OCM).

EXPERIMENTAL

Polystyrene standards were purchased from Polymer Standards Service (Mainz, Germany). The toluene and methyl ethylketone were obtained from Fluka and of puriss. p.a. grade. Both solvents were used as received. The polystyrene solutions were filtered through 0.45-μm polytetrafluoroethylene (PTFE) filters, the organic solvents through 0.22-μm PTFE filters.

The preparation of the PAM standards has been reported elsewhere.[9] PAM samples were dissolved in 0.02 M Na_2SO_4 aqueous solution. The deionized water with a resistivity > 18.2 MΩ/cm (MilliQ-PLUS PFsystem, Waters-Millipore, Lausanne, Switzerland) was filtered through a 0.22-μm nylon membrane filter. The saline-solvent was then filtered through 0.025-μm cellulose-acetate-nitrate filter while the polymer solutions were filtered through 0.45-μm poly(difluorovinylidene) filters (Millipore, Waters-Millipore, Lausanne, Switzerland).

A DAWN DSP multi-angle laser light scattering instrument (Wyatt Technologies SA, Santa Barbara, CA) was used for the light scattering data acquisition. The apparatus was calibrated with toluene. The dn/dc values were determined with a Wyatt Optilab DSP. PS in 2-butanone had a dn/dc of 0.2128 while in toluene the value was 0.1103. PAM in 0.02 M Na_2SO_4 has been reported to be 0.1869 as given in Ref. [9].

RESULTS AND DISCUSSION

Concentration Dependence of Variance

It has been shown in preceding publications[9,14] that the average deviation of the acquired raw data from a low-angle light scattering instrument is concentration dependent. The present investigation has been carried out on an apparatus with multi-angle signal detection, where the intensity of scattered light can be measured simultaneously at several angles. A series of PAM having weight-average molar masses in the range of $1 \cdot 10^5$–$4 \cdot 10^6$ g/mol have been measured in an aqueous sodium sulfate solution. The saline solution was chosen to suppress any polyelectrolyte effect due to hydrolyzed acrylamide which may occupy a fraction of backbone repeating units. For the determination of the RMS radius of gyration, at least three independent dilution series for each molar mass were prepared and measured with the MALLS instrument.

The statistic analysis of the acquired data indicated, that the average deviation of the excess Rayleigh ratio changes with concentration and angle. A three-dimensional plot of R_θ average deviation of six measurements against concentration and angle is depicted in Figure 1. It can be seen that below a certain concentration (here $4.4 \cdot 10^{-5}$ g/mL), the average deviation increases considerably at all measured angles which is attributed to the decreasing signal-to-noise ratio with decreasing polymer concentration. Furthermore, even at polymer concentrations up to $1.3 \cdot 10^{-4}$ g/mL, the average deviation for angles below 60° is above 5%. Only above this concentration and up to $5.6 \cdot 10^{-4}$ g/mL the variances are less than 5%. The average deviation increased again for further concentrated polymer solutions.

The concentration latitude with low variance of the excess Rayleigh ratio is determined by the reduced signal-to-noise ratio at low polymer concentrations and nonreproducibilities in sample preparation and clarification at higher concentrations. While the first effect is instrumental, the solution clarification is highly solvent and molar mass

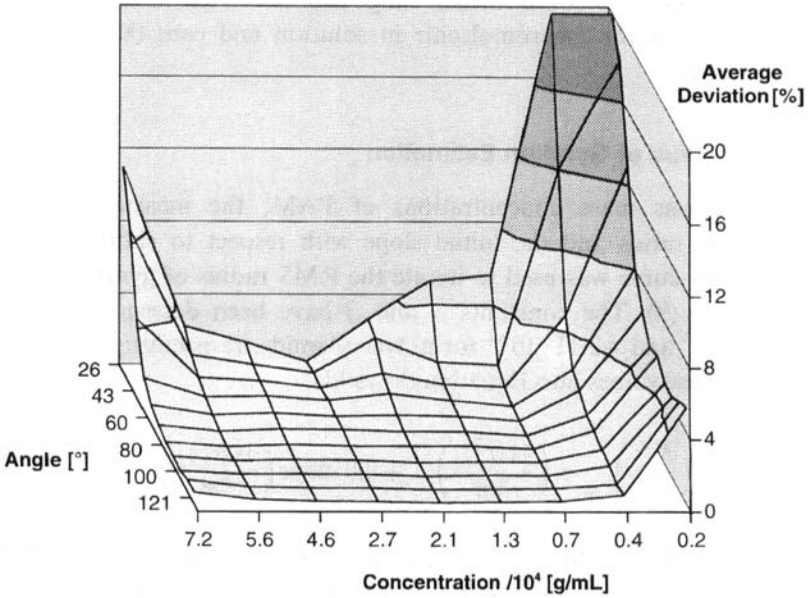

FIGURE 1 Three-dimensional plot of the dependence of the average deviation on angle and concentration for a polyacrylamide of 700 000 g/mol.

dependent with high molar mass water soluble species the most difficult to reproducibly purify. Specifically, the high dielectric constant in aqueous media stabilizes dust and macromolecules to similar extents, given their approximately equal diameter. Therefore, methods based on sedimentation or filtration are compromised by a tradeoff between dust removal and the elimination of polymer form the solution.

The signals at low angles are the most important for the calculation of the initial slope and, thus, for the estimation of RMS radius of gyration. An analysis of the raw data revealed that, in particular for the calculation of the initial slope, only the data acquired within a concentration window yield reliable results in RMS radius of gyration estimation. Over a certain optimum concentration range (e.g., 1.5–$5 \cdot 10^{-4}$ g/mL for a $7 \cdot 10^5$ g/mol PAM sample in 0.02 M Na_2SO_4), the variance is very low even at small angles as was discussed above and can been seen by the valley in Figure 1. One aim of this work was to define the optimum concentration range where the two above mentioned opposing effects of undesired dust and derogatory signal-to-noise ratio yield the lowest variance. It will be demonstrated herein that the optimum concentration range can be related to fundamental properties of the macromolecule in solution and can, therefore, be generalized.

RMS Radius of Gyration Estimation

For various mass concentrations of PAM, the measured excess Rayleigh ratios and the initial slope with respect to $\sin^2\theta/2$ of the measured curve was used to iterate the RMS radius of gyration from Equation (9). The constants α and β have been determined to be $8.18 \cdot 10^{-3}$ and $-2.11 \cdot 10^{-1}$ for polyacrylamide, respectively.[9] Substituting these values into Equation (8) yields

$$\left(\frac{K^*c}{R_\theta}\right)_{\theta=0} = \left(\frac{4k\langle r^2\rangle_z}{3m}\right)^{-1} + 0.01636c\left(\frac{4k\langle r^2\rangle_z}{3m}\right)^{-0.211}. \qquad (9)$$

In Figure 2 the RMS radius determined by applying Equation (9) is plotted versus the used concentration for the data acquisition. The aforementioned differences in raw data variances also influence the variance of the RMS radius of gyration. Only within a concentration

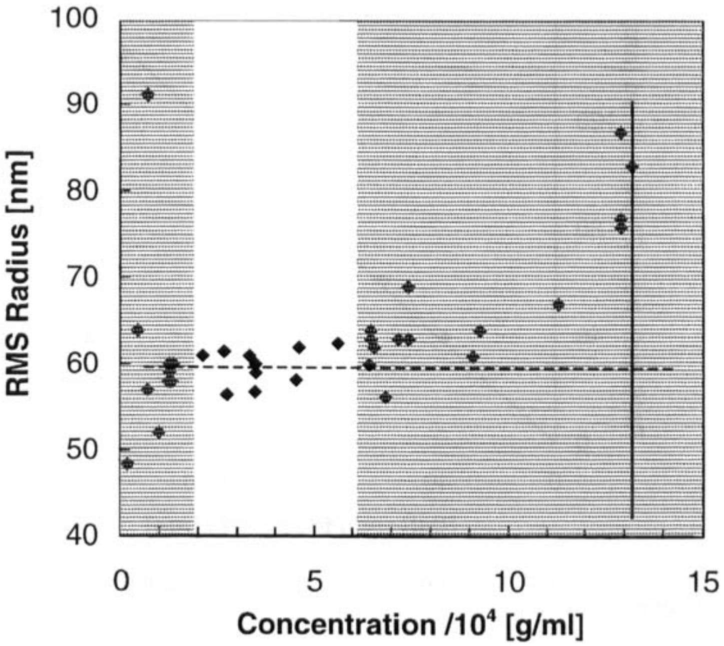

FIGURE 2 Plot of RMS radius calculated with Equation (8) versus concentration of a polyacrylamide standard of 700 000 g/mol.

window (white area in Figure 2) the scattering of the RMS radii is small. At concentrations below $1 \cdot 10^{-4}$ g/mL, the calculated RMS radius of gyration spread widely below and beyond the dashed line which corresponds to the average value obtained from five measurements treated by the Zimm method. Along with an increasing variance, above concentrations of $6.0 \cdot 10^{-4}$ g/mL the calculated RMS radii become larger, which is contradictory to theoretical predictions; in semidilute solutions the scaling theory[21] predicts $\langle r^2 \rangle_z \sim c^{-0.25}$. Scrutinizing the source of the increasing values at higher concentrations was not the subject of this work, though it seems to be due to the tendency of water soluble polymers to form aggregates. If at higher polymer concentrations aggregation of the macromolecules occurred, and these concentrations are used for the extrapolation to $c = 0$, the results from data treated by the Zimm method should be affected in a nonreproducible manner.

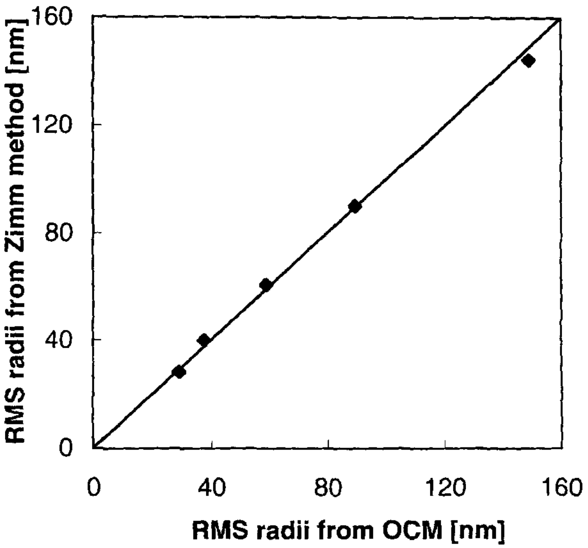

FIGURE 3 Comparison of RMS radii estimated with Zimm method and the one-concentration method.

Figure 3 shows the comparison between the RMS radii of gyration obtained from both the Zimm plot and the one-concentration method. The vertical line in Figure 2 corresponds to the critical overlap concentration c^* calculated following Equation (10). The values obtained with concentrations close to c^* deviate more than 25% from the average value obtained from the Zimm-plot data processing (61 nm) and from the one-concentration method (59 nm). As a consequence it can be concluded that, for accurate RMS radius estimation of PAM samples from Equation (8), the sample concentration should be far below the c^*.

$$c_R^* = \frac{3M_w}{4\pi\langle r_g\rangle^3 N_L}. \qquad (10)$$

Plots such as Figures 1 and 2 have been obtained for each polymer sample. It was observed that the concentration where the lowest variances occurred was a function of the molar mass of the sample, as it was known from preceding investigations.[9,14] However, the data domain of low variance has been extended five times (white area in Figure 2). Therefore, optimum concentration ranges for PAM of various molar mass have been determined where the variance of the RMS radius of gyration has been the smallest. For the application of the one-concentration method, optimum concentration ranges for polyacrylamides with different molar mass are recommended. These have been determined for PAM samples in 0.02 M Na_2SO_4 and are shown in Table I.

The precision of the one-concentration method has been compared to the results of the conventional Zimm method. From Table II it can be concluded that the one-concentration method produces comparable values for the RMS radius along with an improved precision. The one-concentration method resulted in a reproducibility of 3.7% in average, whereas the classical Zimm plots provided 7.2%. More important than the reduced overall average deviation is the fact that for every series of measurements of samples with the same molar mass, the average deviation is smaller when the one-concentration procedure is applied at optimum concentration. It is particularly remarkable that

TABLE I Recommended concentration ranges for the highest precision in the calculation of the RMS radii of PAM in 0.02 M Na_2SO_4

Expected weight average molar mass (g/mol)	*Recommended concentration range* (g/mL)
100000–300000	$5\cdot10^{-4}$–$1.6\cdot10^{-3}$
300000–600000	$2\cdot10^{-4}$–$6\cdot10^{-4}$
600000–1000000	$1\cdot10^{-4}$–$4\cdot10^{-4}$
1000000–3000000	$5\cdot10^{-5}$–$1\cdot10^{-4}$
> 3000000	$1\cdot10^{-5}$–$1\cdot10^{-4}$

TABLE II Comparison of the accuracy in the estimation of the RMS radii by the conventional and the one-concentration method

Polymer M_w	*RMS radius obtained by Zimm plot* (nm)	*Average deviation* (%)	*RMS radius obtained by the one-concentration method* (nm)	*Average deviation* (%)
100000	33, 24, 28	13.0	31, 26, 30	7.5
450000	45, 34, 40	8.4	41, 34, 38	7.6
700000	57, 59, 60, 66	5.5	59, 59, 58, 60	1.4
1500000	87, 90, 93	2.7	89, 90, 90	0.5
3500000	131, 150, 152	6.6	146, 149, 152	1.6
Overall average deviation		7.2		3.7

some data deviate quite largely from the average when analyzed by the dilution technique and processed with the Zimm method. When the same data were analyzed with the one-concentration method, the results appear to be much less erroneous. This supports the inference that low precision data, which has been collected from concentrations apart from the optimum concentration can amplify into poor estimates of molar mass or radius of gyration. Therefore, the one-concentration method can be used as a supplemental procedure to classical data analysis in order to explain apparently spurious results.

Figure 3 shows the estimated RMS radii from the conventional Zimm plot versus the values from the one-concentration method. The weighed linear regression of the data revealed a slope of 0.996 with an R^2 of 0.9986. Except for the highest molar mass, the mean RMS radii obtained from the Zimm plot were higher than those from the one-concentration method. This finding is again consistent with the hypothesis that aggregates are responsible for increasing polymer radii with increasing concentration. These concentrations may be included in the classical extrapolation procedure, however, they are avoided applying the one-concentration method at optimum concentration.

Prediction of Optimum Concentration

It has been found that the concentration where the weight-average molar mass can be estimated with the highest precision depends on molar mass.[9] The same dependence has been observed for the estimation of RMS radii of PAM (Table I). Until this point, the optimum concentration had to be determined empirically for each molar mass and each polymer species. Clearly, the generalization of this method will require the forecast of the optimum concentration range for any linear polymer of molar masses usually applied in light scattering measurements (10^4–10^7 g/mol). A theoretical prediction of the optimum concentration has, therefore, been needed to facilitate the application of the one-concentration method. Figure 4 shows a plot of the excess Rayleigh ratios at $\theta = 0$ versus molar mass. This plot reveals that there is no dependence of the excess Rayleigh ratios, measured at concentrations within the optimum concentration range, on molar mass. In other words, the excess Rayleigh ratios where the lowest variance is obtained have similar values for various molar masses with

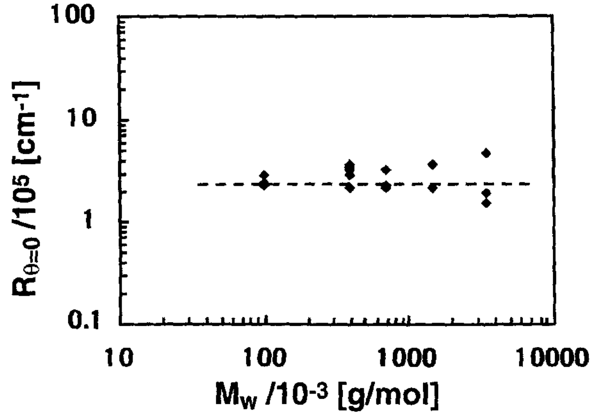

FIGURE 4 Plot of excess rayleigh ratio at $\theta = 0$ as a function of the weight-average molar mass for polyacrylamides in 0.02 M Na_2SO_4.

Rayleigh ratios in the range of $1.5\text{–}4.5 \cdot 10^{-5}\,\text{cm}^{-1}$. Due to the following proportionality,

$$R_{\theta=0} \sim cM_w \tag{11}$$

a small variance in concentration is amplified into a larger variance in the excess Rayleigh ratio with increasing molar mass. Indeed, each point in Figure 4 has been determined at different concentration, though within the optimum concentration range. The average value has been calculated to be $2.6 \cdot 10^{-5}\,\text{cm}^{-1}$. This mean value of $R_{\theta=0}$ at the optimum concentration is used in the following discussion as a constant independent of molar mass. Since the excess Rayleigh ratio is a function of molar mass of the polymer sample (Equation (1)) it is evident that if the Rayleigh ratios at optimum concentration are considered to be constant, the optimum concentration has to vary with molar mass.

To manifest this dependence in an equation, we start from basic relations. For optically isotropic polymers, the relationship between the R_θ and the molar mass can be expressed by[3]

$$R_\theta = K^*McP_\theta[1 - 2A_2cMP_\theta]. \tag{12}$$

Equation (3) can be introduced into Equation (12) to eliminate the second virial coefficient and c can be replaced by c_{opt} when the measurements are executed at optimum concentration, yielding

$$R_\theta = K^* M c_{\text{opt}} P_\theta [1 - 2c_{\text{opt}} \alpha M^{\beta+1} P_\theta]. \tag{13}$$

Since the excess Rayleigh ratio of an angle of zero degree is considered as independent from molar mass at the optimum concentration, it can be replaced by the constant $R_{0,\text{opt}}$ and the particle scattering function P_θ becomes unity. For polydisperse polymer samples Equation (14) follows:

$$\frac{1}{c_{\text{opt}}} = \frac{K^* M_{\text{w}}}{R_{0,\text{opt}}} - 2\alpha M_{\text{w}}^{\beta+1}. \tag{14}$$

Since the Rayleigh ratio and the instrument parameters are held constant, the only parameter that influences the optimum concentration is the molar mass. In Figure 5 the reciprocal concentration is plotted against molar mass. The line represents the values obtained when an excess Rayleigh ratio of $2.6 \cdot 10^{-5}$ is applied in Equation (14). This number has been determined from the plot in Figure 3. The points were obtained from the data of optimum concentrations for different molar masses of PAM from Table I. Figure 5 shows that the experimental points and the calculated values are in very good agreement.

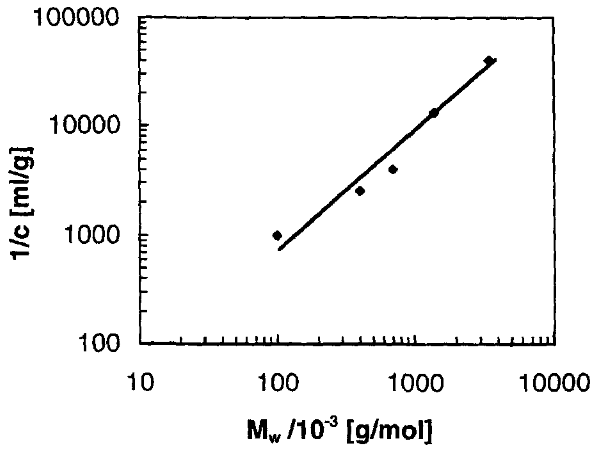

FIGURE 5 Plot of the reciprocal concentration versus molar mass, curve calculated from Equation (14) ($R_0 = 2.6 \cdot 10^{-5}$), whereas the points were obtained from experimental data on polyacrylamides in 0.02 M Na_2SO_4.

The only information that is needed to guess the optimum concentration of any polymer for various molar masses, is the excess Rayleigh ratio where the variance is the lowest. This value is considered as an instrument constant that has been determined in our case for the Wyatt DAWN DSP prior to the application of Equation (14). In this work it has been estimated from measurements of polymer samples of different molar masses. However, even one single molar mass can be sufficient to calculate this constant and predict the optimum concentration for samples of different molar mass. Furthermore, Equation (14) can be used for both weight-average molar mass and root-mean-square radius estimation.

Light scattering theory has been developed with the approximation that a polymer molecule has only one contact to a second polymer chain. This is not the case at concentrations at c^*, the semidilute regime, where the chains start to overlap.[21] In Figure 6 the values of the overlap concentrations for presumed spheres are plotted versus weight-average molar mass (dashed line). In the same graph the recommended optimum concentration ranges (vertical bars) and the calculated optimum concentrations applying Equation (14) (full line) are

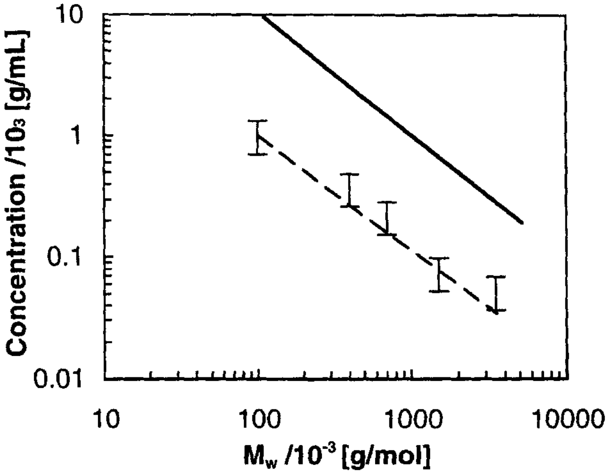

FIGURE 6 Comparison of the optimum concentration for the one-concentration method (full line) and critical overlap concentration c^* (dashed line) of polyacrylamide spheres in 0.02 M Na_2SO_4; the vertical bars represent the found concentrations with low variance.

included. The plot reveals a difference of one order of magnitude between optimum light scattering concentration and critical overlap concentration. The reported optimum concentration range and the calculated concentrations using Equation (14) are far below these concentrations for all investigated molar masses. Therefore, the approximation that only a single contact exists between two polymer chains should be easily fulfilled for concentrations within the optimum concentration range and the assumption that virial coefficients higher than the second order can be neglected is reasonable.

Application to Polystyrene in Organic Solvents

It has been shown with this work that Equation (14) is valid for a linear homopolymer such as PAM in aqueous solution. In order to demonstrate possible application to organic solvents, polystyrene standards have been measured in 2-butanone and toluene. The results of the concentration-dependent RMS radii of gyration are depicted in Figures 7(a) and (b). Along with increasing concentration these data did not show an increase in variance. Only at concentrations where the signal-to-noise ratio was critical, was the variance enlarged. In Table III the results of the PS measurements, obtained by the Zimm method and the one-concentration method, are listed. Included are c^* calculated from Equation (10) and the optimum concentration, calculated from Equation (14) with $R_{0,\mathrm{opt}}$ determined from the preceding measurements of PAM in aqueous solution. Comparison of the data obtained by the Zimm method and those obtained by the one-concentration method shows that the one-concentration method yields precise results for the weight-average molar mass and the RMS radius of gyration estimation.

The predicted optimum concentrations are marked in Figure 7 with arrows. It can be seen that working above and below the optimum concentration range provide similar results. The one-concentration method is revealed to be even more robust with respect to the concentration for PS in organic solvents than for PAM samples, where precise results could only be obtained when distinct concentration ranges were applied. For aqueous solutions the increase in variance with increasing concentration was attributed to dust present during the measurement and the increase in RMS radii with concentration to

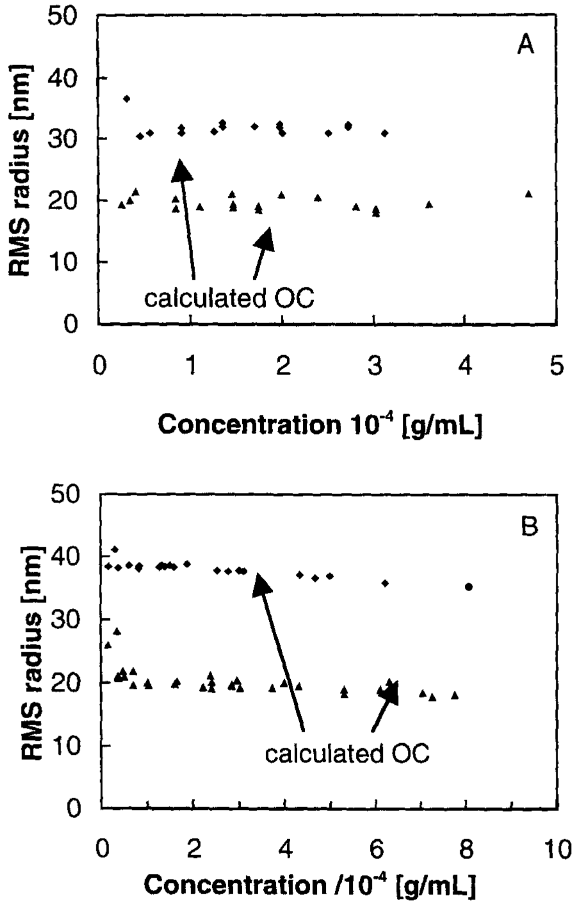

FIGURE 7 RMS radius determined at various concentrations of polystyrene (◆: $M_w = 9 \cdot 10^5$ g/mol, ▲: $M_w = 4 \cdot 10^5$ g/mol) in 2-butanone (A) and toluene (B), "optimum" concentrations (OC) have been calculated from Equation (14) with $R_{0,\mathrm{opt}} = 2.6 \cdot 10^{-5}$.

aggregate formation. Since the stabilization of dust in organic solvents is lower than to aqueous media, due to a lower dielectric constant, it can be expected that measurements in organic solvents are less disturbed by dust, assuming similar purification procedures. This would yield small variances over a large concentration range, as it was the case for PS in both 2-butanone and toluene. Aggregation phenomena are also less known for polystyrene. Conformably, the RMS radii

TABLE III Polystyrene samples characterized with the classical Zimm method and the one-concentration method

Solvent[a]	$M_w \cdot 10^{-3}$ (g/mol)		*RMS radius* (nm)		c_{opt} (g/mL)[d]	c^* (g/mL)[e]
	Zimm[b]	*OCM*[c]	*Zimm*[b]	*OCM*[c]		
MEK	443	441	19	20	$1.89 \cdot 10^{-4}$	$2.18 \cdot 10^{-2}$
MEK	932	936	32	32	$8.39 \cdot 10^{-5}$	$1.13 \cdot 10^{-2}$
TOL	387	384	21	19	$7.23 \cdot 10^{-4}$	$2.22 \cdot 10^{-2}$
TOL	950	931	38	38	$3.08 \cdot 10^{-4}$	$6.73 \cdot 10^{-3}$

[a]MEK: 2-butanone, TOL: toluene. [b]Obtained from classical Zimm method. [c]OCM: one-concentration method, obtained from measurement at OC. [d]Calculated from Equation (14). [e]Calculated from Equation (10) (OCM values).

of gyration show a slight tendency to decrease with increasing concentration, as predicted from the scaling theory.[21] The application of Equation (14) still provides an indication in which concentration range reliable and precise results can be obtained for an expected molar mass, though this is found to be more important for PAM in aqueous solvents than for PS in organic solvents. Moreover, the data in Table III reveal that the optimum concentration range has been more than one order of magnitude lower that the critical overlap concentration for both PAM and PS. Working at or near the optimum concentration range ensures that the polymer concentration of PAM in aqueous solution and PS in either 2-butanone or toluene is sufficiently low to carry out the measurements more than one order of magnitude below c^*. Also for PS, applying the one-concentration method economizes polymer product, solvent and time, concomitant with enhanced precision of the measurements.

CONCLUSIONS

The one-point method, from which weight-average molar mass can be predicted with low-angle light scattering measurements at a single concentration, has been transformed to estimate the root-mean-square radius from multi-angle laser light scattering data. It has been found that the variance of the excess Rayleigh ratio, as well as the variance of the calculated RMS radius, depend on the concentration for a given molar mass. The precision in the estimation of the RMS radius could be improved twofold to 3.7% by operating within the optimum concentration range. The excess Rayleigh ratios of polymers with different molar masses measured at optimum concentration has been found to vary only to a small extent. Based on this fact, a mathematical description of the molar mass dependence of the optimum concentration is reported for the first time. This can be used to predict the optimum concentration for molar mass and RMS radius estimation of linear homopolymers. Furthermore, it has been found for PAM in 0.02 M Na_2SO_4 and PS in toluene and 2-butanone that the optimum concentration is one order of magnitude lower than the critical overlap concentration for presumed spheres.

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