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A Novel One-concentration Method for Improved Multi-Angle Laser Light Scattering

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SUMMARY: A novel data interpretation method is presented which is derived from weighted least squares analysis. Given the steep dependence of the Rayleigh factor on concentration, a Zimm-plot based regression of weight average molar mass and the RMS radius of gyration is strongly influenced by data over an optimum concentration range, which can be quite narrow for some polymer-solvent combinations. The "one-concentration method" exploits this sensibility to improve the precision in molar mass and radius of gyration measurements to ±4%. The theoretical prediction of the optimum concentration is included. The one-concentration method is applied to polymers in organic solvents as well as to water-soluble polyelectrolytes.

Introduction

The intensity of light scattered by a system of independent particles is, at a given mass concentration, proportional to their molar mass. Debye was the first to apply this to the characterization of polymers[1,2] for the estimate of weight-average molar mass and an important size parameter of particles in solution, the *z*-averaged root mean square (RMS) radius of gyration. 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:

$$\frac{K^*c}{R_\theta} = \frac{1}{M_w P_\theta} + 2A_2c + 3A_3c^2 \ldots \tag{1}$$

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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 second and higher order terms in the virial expansion are negligible. A double extrapolation to $\theta=0$ and $c=0$ yields Equation (2) from which the weight-average molar mass can be determined:

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

Zimm published this technique in 1948 and it is still applied for the determination of molar mass and RMS radius of gyration of polymers, which are soluble in organic and aqueous solvents5-8). 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 combined with highly precise data, since the variances of different concentrations are not identical, and can differ by two orders of magnitude9). 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 calculations10,11), altering the graphical treatment12), applying a one point method9,13-15), or by combining low angle laser light scattering with sedimentation techniques16). A weighted least squares analysis, which would be obvious, is quite cumbersome experimentally.

The purpose of the present work has been to evaluate the differences of the one-concentration method9,13-15,17) applied to an organically soluble polymer or a water-soluble polymer. The measurements, which were also analyzed by the classical Debye and Zimm-technique, have been conducted with polystyrene (PS) and polyacrylamide (PAM). The results of RMS radius of gyration and molar mass estimation are considered. PAM is mainly applied in aqueous solution for water treatment applications18-20), to reduce soil erosion in agriculture21), for enhanced oil recovery22) and as drag reduction agent23). Polystyrene, often considered as a model macromolecule, has been the subject of many investigations over the past fifty years4,10,24,25).

Molar Mass Estimation

Hunkeler *et al.*9,17) showed that 50% of the variance in light scattering measurements is due to the estimation of the second virial coefficient from the dilution of a base sample. They conducted their measurements with a low angle laser light scattering apparatus (LALLS) at a measuring angle of 4.8° and R_θ can be approximated by $R_{\theta=0}$. The weight-average molar mass could be estimated more precisely with the measurement of the excess Rayleight ratios at a single concentration given the empirical dependence of the second virial coefficient on molar mass expressed by Equation (3).

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

Polydispersity effects demand only a negligible correction if the most probable distribution is considered9). 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 determined either empirically or via the Mark-Houwink-Kuhn-Sakurada relation26). In a good solvent, the Mark-Houwink-Kuhn-Sakurada exponent will be approximately between 0.7 and 0.8. Since β=a-1, with *a* the Mark-Houwink-Kuhn-Sakurada exponent, β will have a value between -0.2 and -0.3 as is generally observed. It has also been demonstrated that for systems in a theta solvent, the values of *a* and β revert to 0.5 and -0.5 respectively14). Given that the values of α and β are established from the correlation of multiple sets of individual light scattering measurements (often tens or hundreds instead of only 4 or 5 with a classical dilution method), it is reasonable to expect that the accuracy in the estimate of the second virial coefficient is dramatically improved with the one-concentration method compared to classical dilution techniques such as Debye or Zimm plots. Distinct values are available for several polymer-solvent systems[9]. Equation (4) can, therefore, be used to estimate weight-average molar mass from the measurement of the excess Rayleigh ratio of a single concentration[9,13-15,17].

It has also been found that the variance changes with concentration and the optimum concentration 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-concentration method required much less time, sample and solvent, since measurements at only one-concentration were necessary.

z-Average Mean Square Radius of Gyration

The reduction of scattering intensity is a function of the angle, with P_θ in Equation (5) approaching unity when θ verges upon 0 and can be expressed as:

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

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 (RMS) *z*-average 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 $\sin^2(\theta/2) \rightarrow 0$, 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 $k = 2\pi n_0/\lambda_0$

$$m = \frac{d\dfrac{K^*c}{R_\theta}}{d[\sin^2(\theta/2)]} = \frac{1}{M_w}\frac{4k^2}{3}\left\langle r^2 \right\rangle_z \qquad (6)$$

which can be substituted in Equation (4) to yield:

$$\left(\frac{K^*c}{R_\theta}\right)_{\theta=0} = \left(\frac{4k^2\left\langle r^2\right\rangle_z}{3m}\right)^{-1} + 2c\alpha\left(\frac{4k^2\left\langle r^2\right\rangle_z}{3m}\right)^{\beta} \qquad (7)$$

As the left side of Equation (7) is obtained from measured data by extrapolating to $\theta=0$, the mean square radius of gyration can be regressed from this relation in the same way as the weight-average molar mass from Equation (4). Therefore, Equation (7) is an expression, which can be used to improve the precision of $<r>_z$ estimation, as will be demonstrated later. This equation is not restricted to the slope *(m)* of the points extrapolated to zero concentration usually used in determination of the RMS radius of gyration. In principle any concentration can be employed15). 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 (7) reduces to Equation (2). "One-point method" has been replaced by the term "one-concentration method" since several points, at least two, must be measured for RMS radius of gyration calculation.

EXPERIMENTAL

Materials

Polystyrene (PS) standards were purchased from Polymer Standards Service (Mainz, Germany). The toluene and 2-butanone 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.

Solution Preparation

The preparation of the PAM standards has been reported elsewhere9). 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 polydifluorovinyliden filters (both Millipore, Waters-Millipore, Lausanne, Switzerland).

Light Scattering

The low angle light scattering measurements were conducted with a Chromatix KMX-6 LALLS photometer, the cell length being 15 mm and a field stop of 0.2. This matches an average scattering angle of 4.8°. A DAWN DSP multi-angle laser light scattering instrument (Wyatt Technologies SA, Santa Barbara, USA) was used for the light scattering data acquisition. The apparatus was calibrated with toluene. Polystyrene samples and a series of PAM having weight-average molar masses in the range of $1 \cdot 10^5$ to $4 \cdot 10^6$ g/mol have been measured. For the estimation of the molar mass and the RMS radius of gyration, at least three independent dilution series for each molar mass were prepared and measured with the MALLS instrument. The dn/dc values were determined with a Wyatt Optilab DSP (Wyatt Technologies SA, Santa Barbara, USA). PS in 2-butanone had a dn/dc of 0.213 mL/g while in toluene the value was 0.110 mL/g. PAM in 0.02 M Na_2SO_4 has been reported to be 0.187 mL/g Ref.9).

RESULTS AND DISCUSSION

Variance of the Excess Rayleigh Ratio

From light scattering investigations carried out on a low-angle light scattering instrument, the average deviation of the recorded raw data has been revealed to be concentration dependent9). At very low polymer concentrations, the scattering intensity is small which resulted in a poor signal-to-noise ratio and caused an enormous increase in variance at low concentrations. At high polymer concentrations the filtering procedure of the polymer prior to the measurements was suspected to be the source of irreproducebilities in sample preparation and clarification. An obscured baseline and unreliable measurements were observed. As a consequence it has been found that the variance of scattering measurements was a function of the polymer concentration. The concentration with the smallest variance was preferred when the one-concentration method was applied and lower variances in molar mass estimations were obtained for PAM samples in aqueous saline solution.

A three dimensional plot of R_θ average deviation of six measurements versus concentration and angle is depicted in Fig. 1a (PAM) and 1b (PS). It can be seen that below a certain concentration the average deviation increases considerably at all measured angles which is attributed to the decreasing signal to noise ratio with decreasing polymer concentration. This is observed for both PAM and PS samples. Furthermore, even at polymer concentrations up to $1.3 \cdot 10^{-4}$ g/mL of PAM the average deviation for angles below 60° is above 5%. Only for higher concentrations and up to $5.6 \cdot 10^{-4}$ g/mL the variances are less than 5%. For further concentrated PAM solutions the average deviation increased again whereas the average deviation of PS measurements remained constant. The concentration range with low variance for PAM is determined by the reduced signal to noise ratio at low polymer concentrations. At high polymer concentrations the solution clarification is difficult to execute reproducibly which is confirmed by the increase in variance at high PAM concentration.

Data analysis revealed that, in particular for the calculation of the initial slope, only the data acquired within a concentration window yielded reliable results in molar mass and RMS radius of gyration estimation. The signals at low angles are the most important for the extrapolation to $\theta=0$ and calculation of the initial slope and, thus, for the estimation of RMS radius of gyration. For PAM a certain optimum concentration range (e.a. $1.5\text{-}5 \cdot 10^{-4}$ 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 Fig. 1a. The determination of the optimum concentration range where the two above mentioned opposing effects of undesired dust and derogatory signal to noise ratio yield the lowest variance is of importance for the water-soluble PAM.

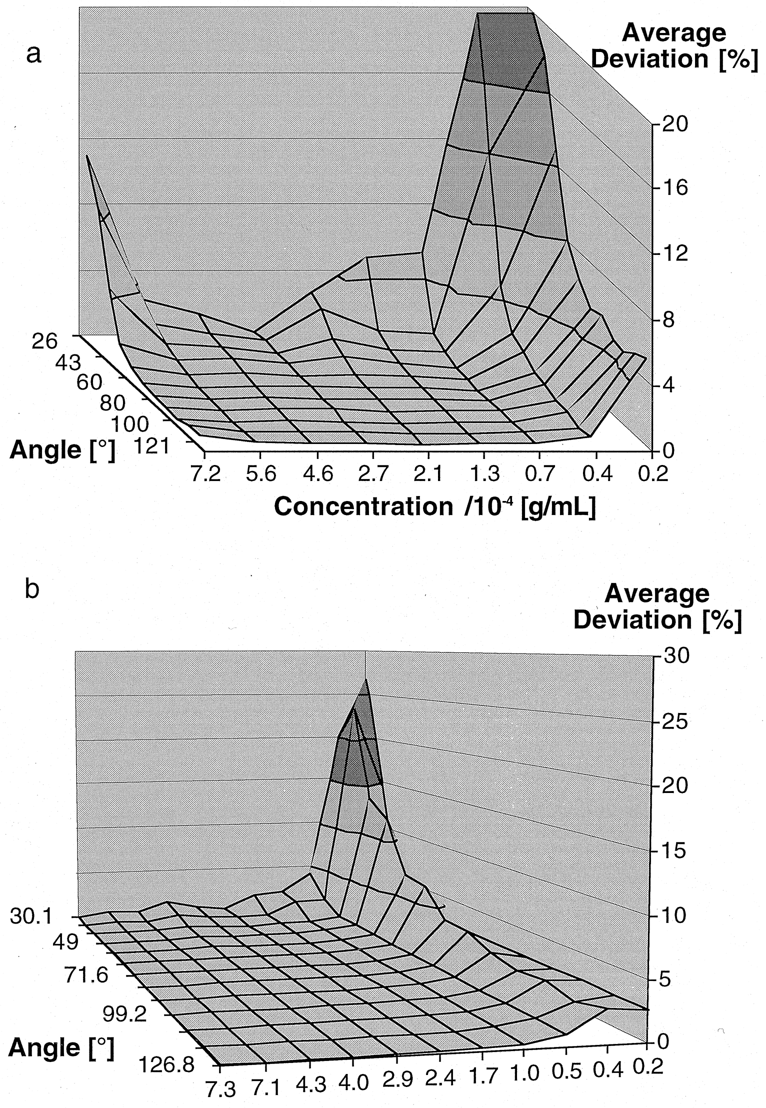

Fig. 1: Dependence of the excess Rayleigh ratio average deviation on both the angle and concentration for (a) PAM in aqueous solution and (b) PS in toluene.

Polystyrene likewise revealed a severely increased average deviation at low concentrations (below $5 \cdot 10^{-5}$ g/mL)*, where the signal-to-noise ratio is inopportune. Contrary to PAM the PS samples did not show this tendency at high concentrations. Over more than one order of magnitude in concentration no increase in variance was observed up to the highest measured concentration. This lead to the conclusion that the solution clarification is highly solvent dependent with high molar mass water-soluble species the most difficult to purify. A polymer soluble in an organic solvent such as PS are much less affected from purification difficulties and should yield reliable results over a broad concentration range. Fig. 2 demonstrates the equivalence of molar mass estimation by the Zimm and the one-concentration method over more than three orders of magnitude. Values for α and β were taken from Ref.9) for the new one-concentration method, whereas A_2 was determined in the classical way from a dilution series of 4 to 6 concentrations.

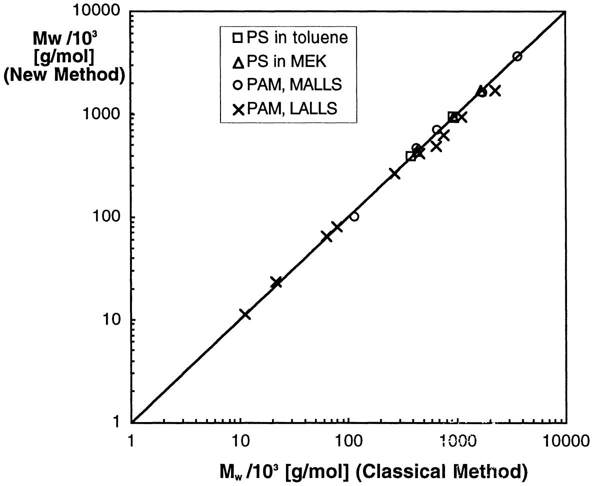

Fig. 2: Comparison of weight average molar mass estimated with a classical method (O, Δ, □: Zimm; ×: Debye) and one-concentration method (New Method).

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* The absolute values can not be compared between PAM and PS due to the differences in K*

Estimation of RMS Radius of Gyration

The light scattering measurements on PAM and PS have also been used to estimate the RMS radius of gyration. In Fig. 3 and 4 the RMS radius of gyration determined by applying Equation (8) is plotted versus the employed 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 window (white area in Fig.3) the precision in the estimation of the RMS radii is reasonable. At concentrations below $1\cdot10^{-4}$ 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 $6.0\cdot10^{-4}$ g/mL, the calculated RMS radii become larger, which is contradictory to theoretical predictions; in semidilute solutions the scaling theory27) expect $\langle r^2\rangle_z \sim c^{-0.25}$. 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 aggregates28). 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 an irreproducible manner.

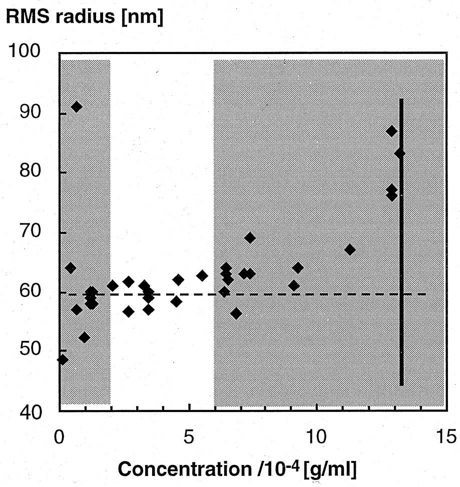

Fig. 3: RMS radius of gyration determined at various concentrations for PAM (M_w=$7\cdot10^5$ g/mol) in 0.02 M Na_2SO_4 solution.

The results from Fig. 4 reveal that, for polymers soluble in organic solvents, the optimum concentration range is much larger with RMS radii of gyration estimated precisely over one order of magnitude in concentration.

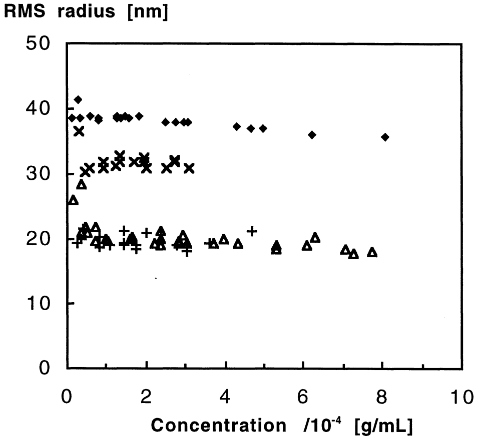

Fig. 4: RMS radius of gyration determined at various concentrations of PS in methylethylketone (+: M_w=4·10^5 g/mol; ×: M_w=9·10^5 g/mol) and toluene (Δ: M_w=4·10^5 g/mol ◆: M_w=9·10^5 g/mol).

Precision of One-concentration Method

The precision of the one-concentration method has been compared to the results of the conventional Zimm method. From Fig. 5 it can be concluded that the one-concentration method produces comparable values for the RMS radius of gyration. However, the one-concentration method resulted in a reproducibility of 3.7% in average, whereas the classical Zimm-plots provided 7.2%. Equally important to 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. Some data deviate quite largely from the average when analyzed by the dilution technique and processed with the Zimm method. Analyzed with the one-concentration method, the same data 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 subsidiary procedure to classical data analysis in order to explain apparently spurious results[17]).

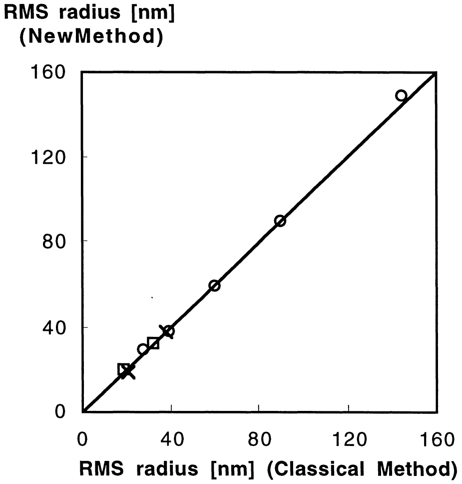

Fig. 5: Comparison of RMS radius of gyration estimated with a classical method (○: PAM; □: PS in toluene; ×: PS in 2-butanone) and one-concentration method (New Method).

Prediction of Optimum Concentration

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[15]). Clearly, the optimum concentration can be determined empirically for each molar mass and each polymer species. A 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 is needed to facilitate the application of the one-concentration method. Fig. 6 shows a plot of the excess Rayleigh ratios at $\theta=0$ versus molar mass. The data has been collected within the optimum concentration range ($R_{0,\ \mathrm{opt}}$) for each molar mass, thus for each molar mass a different polymer concentration was used. This 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 Rayleigh ratios in the range of 1.5 to 4.5·10^{-5} cm^{-1}.

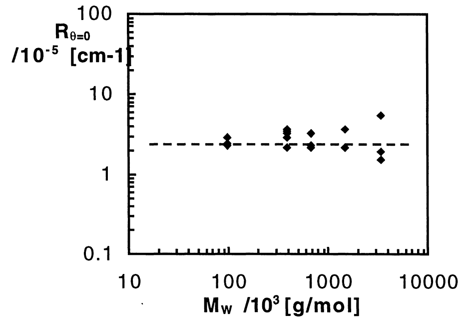

Fig. 6: Plot of excess Rayleigh ratio at θ=0 as a function of the weight-average molar mass for PAMs in aqueous solution.

Due to the following dependence of the excess Rayleigh ratio on the concentration3),

$$R_{\theta=0} = K^* Mc\left[1 - 2A_2cM\right] \tag{8}$$

a small variance in concentration is amplified into larger variance in the excess Rayleigh ratio with increasing molar mass. Each point in Fig. 6 has been determined at a different concentration, though within the optimum concentration range. The average value has been calculated to be 2.6·10^{-5} 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, 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 started from basic relations. For optically isotropic polymers the relationship between the R_θ and the molar mass can be expressed by3):

$$R_\theta = K^* McP_\theta\left[1 - 2A_2cMP_\theta\right] \tag{9}$$

Equation (3) can be introduced into Equation (9) to replace the second virial coefficient. The optimum concentration c_{OPT} substitutes c when the measurements are executed at optimum concentration, yielding:

$$R_\theta = K^* M c_{OPT} P_\theta \left[1 - 2 c_{OPT} \alpha M^{\beta+1} P_\theta\right] \tag{10}$$

The particle scattering function P_θ becomes unity at an angle of zero degree. Since the excess Rayleigh ratio at this angle and at c_{OPT} is considered to be independent from molar mass it can be replaced by the constant $R_{0,OPT}$. For polydisperse polymer samples follows (by the use of $1/(1+x) \approx 1-x$) :

$$\frac{1}{c_{OPT}} = \frac{K^* M_w}{R_{0,OPT}} - 2\alpha M_w^{\beta+1} \tag{11}$$

Since the Rayleigh ratio and the instrument parameters are held constant, the only variable that influences the optimum concentration is the molar mass. In Fig. 7 the concentration is plotted against molar mass. The dashed line represents the values obtained when an excess Rayleigh ratio of $2.6 \cdot 10^{-5}$ cm^{-1} is applied in Equation (11). This number has been determined from the plot in Fig. 6. The vertical bars represent the empirically found optimum concentrations for various molar masses of PAM.

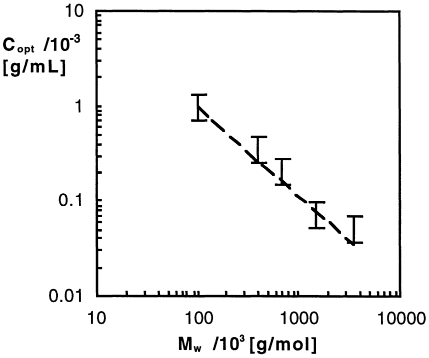

Fig. 7: The empirically found optimum concentrations (vertical bars) and the theoretically predicted optimum concentrations (dashed line) for PAM in aqueous solution.

The optimum concentration can be calculated with Equation (11) over a broad range of molar masses of any polymer. The excess Rayleigh ratio, where the variance is the lowest, need to be determined (e.g. $2.6 \cdot 10^{-5}$ cm^{-1}) and can be considered as an instrumental constant. The instrumental constant will differ from apparatus to apparatus, depending on laser power, frequency and geometrical set-up of the light scattering device. However, the constant is independent from the polymer-solvent combination. One single molar mass can be sufficient to establish the concentration-molar mass relation, although in this work it has been estimated from measurements of polymer samples of different molar masses. Furthermore, Equation (11) can be used for both weight-average molar mass and RMS radius of gyration estimation.

Polyelectrolytes

To date no attempts have been reported to apply the one-concentration method to polyelectrolytes. Measurements of poly(2-trimethylammonium ethyl methacrylate chloride), PTMAM, in 1 M NaCl reveal congruity in molar mass and RMS estimation between the one-concentration method (Fig. 8) and the results from the Zimm method (M_w=$4.8 \cdot 10^6$g/mol, RMS radius of gyration=145 nm). The values for α and β are provided in Table 1. The predicted optimum concentration was calculated as to $2.32 \cdot 10^{-5}$ g/mL. The molar mass and the RMS radius of gyration obtained between $2 \cdot 10^{-5}$ g/mL and $5 \cdot 10^{-5}$ g/mL deviate only marginally from the results gained from the Zimm-plot. It can, therefore, be concluded that also for this polyelectrolyte, the prediction of the optimum concentration is feasible employing Equation (11).

Table 1. Values of α and β in the Expression $A_2=\alpha \cdot M^\beta$ for some polyelectrolytes.

Polymer	α (mol·mL·g^{-2})	β	Reference
Poly(diallyldimethylammonium chloride) in 1 M NaCl	$1.61 \cdot 10^{-3}$	-0.36	29)
Poly(2-trimethylammonium ethyl methacrylate chloride) in 1 M NaCl	$8.25 \cdot 10^{-3}$	-0.26	30), This Work
Poly(2-acrylamido-2-methylpropanesulfonate) in 0.5 M NaCl	$1.67 \cdot 10^{-2}$	-0.30	31)
Poly(acrylic acid) in 1 M NaCl	-	-0.37	32)

Similar to the PAM experiments, the results of both molar mass and RMS radius of gyration increase with concentration. Again, the aforementioned tendency of water-soluble polymers to create aggregates might be responsible for this occurrence. However, additional measurements are needed to validate these conclusions. Further experiments will include cationic and anionic synthetic polymers such as poly(diallyldimethylammonium chloride) and poly(acrylic acid) whereas α for the latter has not been determined to date. The method has also been tested against copolymers[14]).

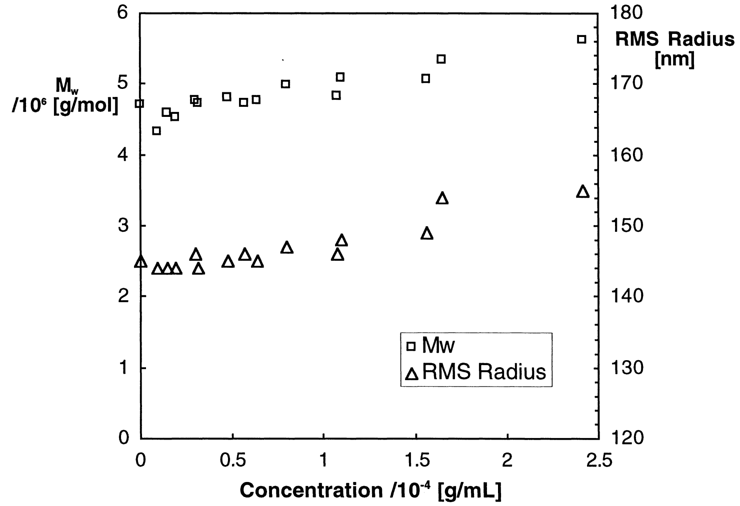

Fig. 8: Weight-average molar mass and RMS radius of gyration of a poly(trimethylammonium ethyl methacrylate) sample obtained with the one-concentration method at various concentrations (results from Zimm-plot: M_w=4.8·10^6g/mol, RMS=145 nm).

Conclusion

A novel method for the estimation of weight average molar mass and the root mean square radius of gyration by light scattering experiments of only a single concentration has been developed. The method used a theoretical estimate of the second virial coefficient and has been tested on nonionic and charged water-soluble polymers as well as on polystyrene in two organic solvents. The prediction of the optimum concentration allows the identification of the minimum variance concentration at which accurate and precise results are obtained.

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