LIGHT SCATTERING OF PARTICLES EMBEDDED IN SOFT HYDROGEL

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

This study is concerned with soft polyacrylamide gels in which are embedded either polystyrene latexes or block copolymer micelles with polystyrene cores and poly(methacrylic acid) shells. We have found that light scattering provides useful structure information about the systems. For polystyrene latexes, both molar mass and radius of gyration do not change during the embedding in the hydrogel; for block copolymer micelles, molar mass does not change, while the size decreases upon immobilization. In all cases, the second virial coefficient is very small and overshadowed by the turbidity of the sample. For large particles with narrow particle size distribution, a combination of Guinier and Zimm plots has been used for obtaining the particle size and molar mass.

While light scattering from solutions has been studied exhaustively[1–3], static light scattering of particles in nonfluid media has been sorely neglected. Nevertheless, such systems are theoretically interesting and possibly important in practice.

   This study is concerned with soft polyacrylamide (PAM) gels in which polystyrene latexes or block copolymer micelles with polystyrene cores and poly(methacrylic acid) shells are embedded. The former system has been studied recently using quasielastic light scattering[4]. We wanted to see whether embedding of the particles affected fluctuations of the concentration of particles – the underlying source of light scattering. Some experimental difficulties arise because of the nature of the system. First, the intensity of light scattered by the embedded particles must be high enough to exceed the intensity of the hydrogel background scattering. However, an increase in scattering intensity leads to high turbidity and significantly interferes with the observation of the concentration dependence of light scattering. Second, for big particles with a spherical shape

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and a narrow particle size distribution, the angular dependences of the inverse scattering intensity are strongly curved upwards. The radius of gyration cannot be obtained from the conventional Zimm plot. A modified plot[5], i.e., combination of Guinier and Zimm plots, leads to a more convenient interpretation of light scattering data, as demonstrated recently for solutions of particles[6] prepared by dispersion polymerization.

EXPERIMENTAL

Materials

Block copolymers of styrene and methacrylic acid were synthesized in our laboratory and were described earlier[7]. Molar masses of the diblocks under study, SA-23 and SA-24, are $55 . 10^3$ and $40 . 10^3$ g mol^{-1}, respectively, and their mass fractions of styrene units are 0.60 and 0.55, respectively. The characterization of copolymer micelles was reported elsewhere[8,9]. Molar mass and size of micelles depend on the way of their preparation[10]. In this study, micellar solutions were formed by dissolving the block copolymers in a mixed solvent of 80 vol.% dioxane and 20 vol.% water. This solution was freeze-dried and the micelles were redissolved in pH 7.0 phosphate buffer solution. Resulting values of molar mass and radius of gyration (Table I) are much larger than the values of micelles prepared by the dialysis method[11].

Polystyrene (PS) latexes were purchased from Polysciences Inc. The size of the PS latexes ranges from 60 nm to 200 nm in diameter. The polydispersity of PS latexes was examined by quasielastic light scattering using the cumulant method[12] and was found to be less than 0.05.

Acrylamide was obtained from Aldrich Company and was recrystallized three times from acetone. All other chemicals were purchased from reputable suppliers and used as received.

Embedding Polymer Particles in the Hydrogel

Typically, 5 ml of a dilute solution of polymer particles (latexes or micelles, concentration ca 10^{-4} g ml^{-1}) and 10 ml 4% aqueous acrylamide solution (containing 20 mg of N,N'-methylenebisacrylamide, a crosslinking agent) were mixed in a light scattering cell and their light scattering was measured. 2 ml of 3% potassium peroxydisulfate solution and 10 µl of N,N,N',N'-tetramethylethylenediamine were then added to the solution as an initiator and a catalyst, respectively. The solutions were mixed using a micromagnetic stirrer. The gelation occurred within a few minutes after adding the initiator. The reaction mixture was kept under nitrogen at room temperature overnight to ensure the completeness of the reaction. The resulting gel was then studied by the light scattering again. All solutions were filtered before mixing to avoid dust particles.

Qusielastic Light Scattering (QELS)

A Brookhaven Instrument BI-2030, multiangle scattering goniometer with a He–Ne laser light source, was used to measure the hydrodynamic radii and polydispersities of polystyrene latexes and polystyrene-*block*-poly(methacrylic acid) micelle solutions.

Static Light Scattering

The static light scattering measurements were performed on a modified Fica 50 photometer equipped with a mercury lamp, a neutral filter, and a polarizer providing vertically polarized incident light at $\lambda_0 = 546$ nm. The scattered light was registered by a laboratory photometer and its output was

measured by a Hewlett–Packard multimeter (model 3478A) interfaced to a computer. All measurements were performed at 25 °C.

Refractive index increments, dn/dc, were measured with a Brice–Phoenix differential refractometer at $\lambda_0 = 546$ nm; dn/dc values for PS latexes, SA-23 and SA-24, both solutions and gels, were 0.248, 0.180 and 0.188 $cm^3\,g^{-1}$, respectively.

Turbidity Measurement

The turbidities of polymer particles were measured on a Hewlett–Packard 8451 Diode Array UV-VIS Spectrometer. The apparent absorption coefficient was determined at $\lambda_0 = 546$ nm.

DATA ANALYSIS FOR STATIC LIGHT SCATTERING

The intensity of light scattered by polymer solutions is commonly expressed in terms of angular-dependent Rayleigh ratio R_θ, which is related to the scattering vector q and concentration c as

$$Kc/R_\theta = (1 + r_g^2 q^2/3 + \ldots)/M + 2A_2 c + \ldots \quad , \tag{1}$$

TABLE I
Light scattering of polystyrene latexes and copolymer micelles in 4% aqueous acrylamide solutions and PAM gels

Parameter	Polystyrene latexes			Copolymer micelles	
	PS-1	PS-2	PS-3	SA-23	SA-24
Solutions					
r_h, nm	38.2	72.9	117.8	94.5	88.5
r_g, nm	29.8	54.4	80.4	84.6	57.2
r_g/r_h	0.78	0.75	0.68	0.90	0.64
ε, $cm^2\,g^{-1}$	763	4 100	9 200	304	207
$A_2 \cdot 10^7$, mol $cm^3 g^{-2}$	–1.5	–0.10	–3.2	–0.48	5.8
$M_w \cdot 10^{-6}$, g mol^{-1}	135 148[a]	1 400 1 030[a]	5 120 4 330[a]	301 –	101 –
Gels					
r_g, nm	33.8	55.1	82.9	56.7	40.8
$A_2 \cdot 10^7$, mol $cm^3\,g^{-2}$	–2.4	–0.68	–0.2	–2.6	5.95
$M_w \cdot 10^{-6}$, g mol^{-1}	131	1 400	5 310	282	136

[a] Calculated from Eq. (6).

where M is the molar mass, r_g is the radius of gyration, A_2 is the second virial coefficient, $q = 4\pi n \sin(\theta/2)/\lambda_0$, $K = 2\pi^2 n^2 (dn/dc)^2/(\lambda_0^4 N_A)$ is a constant characteristic of the polymer–solvent system, n is the refractive index, θ is the scattering angle and N_A is the Avogadro constant. The higher terms in c and q^2 are neglected in Eq. (*1*).

For a turbid medium, the observed intensity, i, of scattered light is weakened by the turbidity of the sample:

$$i = i_0 \, e^{-\tau l} \;, \tag{2}$$

where l is the length through which the light (the primary beam before being scattered plus the scattered beam) travels in the scattering cell, τ is the turbidity of the sample, depending on concentration as

$$\tau = \varepsilon c \;, \tag{3}$$

where ε is the apparent absorption coefficient. Figure 1 shows the plot of turbidity of polymer particles in 4% aqueous acrylamide solutions as a function of particle concentration. From the slope of this plot we obtained values of ε.

We have shown previously[13] that neglecting the turbidity effect leads to an overestimation of the second virial coefficient A_2. This becomes significant when A_2 is very small – a typical case with large compact particles. The turbidity, however, does not
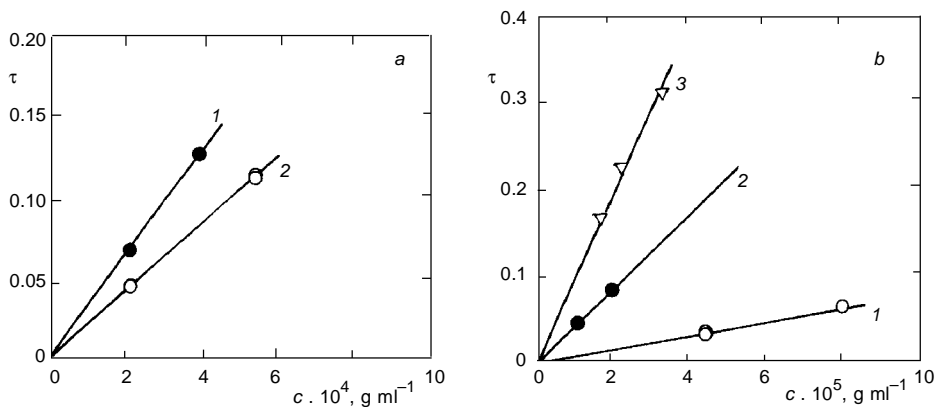

FIG. 1

Plot of turbidity of polymer particles in 4% aqueous acrylamide solution as function of concentration. *a* Copolymer micelles: *1* SA-23, *2* SA-24; *b* copolymer latexes: *1* PS-1, *2* PS-2, *3* PS-3

influence the measured values extrapolated to vanishing concentration, i.e., molar mass and radius of gyration. In our study, we corrected the measured value of R_θ by multiplying it by the term $e^{\varepsilon c l}$. We used $l = 2$ cm, i.e., the diameter of our scattering cell.

For a system consisting of big spherical particles with a narrow particle size distribution, the angular dependences in the common Zimm plot are curved strongly upwards and the extrapolation for obtaining r_g becomes difficult. In this case, it is worthwhile to recall that Guinier showed that, for large compact particles, the light intensity decreases more or less exponentially with q^2:

$$i_\theta = i_{\theta=0} \exp\left(-r_g^2 q^2/3\right) \ . \tag{4}$$

We have utilized the Zimm idea for graphic double extrapolation and plotted $\ln (Kc/R_\theta)$ vs $\sin^2(\theta/2) + kc$. In this plot, the dependence on q^2 should be only slightly curved:

$$\ln (Kc/R_\theta) = -\ln M + r_g^2 q^2/3 + 2 A_2 M c + \dots \ . \tag{5}$$

In the traditional Zimm plot, both slope and intercept are needed for the evaluation of r_g^2 (cf. Eq. (1)). In the modified plot, however, only the slope with respect to q^2 is needed.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of scattering intensity of PAM hydrogels on the scattering angle at several concentrations of the gel. The intensity increases gradually with the increase in concentration. No abrupt change of scattering intensity was observed at gelation point, in contrast to common rheological measurements. The intensity of the hydrogel background scattering ranges from 1/20 to 1/3 of the intensity caused by the polymer particles. Note that the concentration of PAM in our embedding experiments was 0.0235 g ml^{-1} corresponding to curve *4* in Fig. 2. We have subtracted this "solvent" scattering from the total in our light scattering measurements. Table I lists data collected from both quasielastic and static light scattering experiments performed before and after the polymerization of acrylamide.

For polystyrene latex of moderate size, i.e., $r_g < 100$ nm, the conventional Zimm plot is still convenient. Figures 3 and 4 are typical Zimm plots for polystyrene latex of moderate size, PS-2, before and after embedding in the polymer gel. The plot is slightly curved upwards, indicating particles with spherical shape having a narrow size distribution. Figures 3 and 4 are essentially identical. This means that the sizes and molar masses of the latexes are not affected by the gelation process and that no aggregation

of the particles takes place. This also means that the inhomogeneities (fluctuations) of latex particle concentration have the same magnitude, i.e., they affect their light scattering behaviour in the same way, no matter whether they are fluctuating fast (in solution) or are showed, even frozen, in gels.

The dependence of Kc/R_θ on $\sin^2(\theta/2)$ (Fig. 5) for a large size polystyrene latex, PS-3, embedded in the hydrogel is strongly curved upwards and the extrapolation for
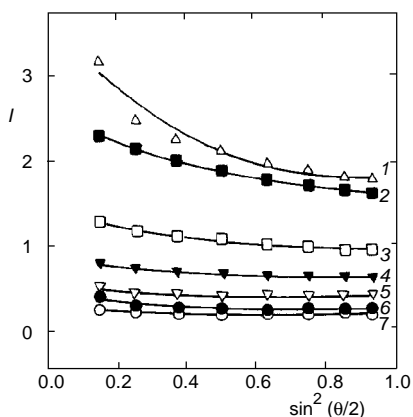

Fig. 2

Scattered intensity I (relative scale) vs $\sin^2(\theta/2)$ for various concentrations of polyacrylamide gel in g ml^{-1}: *1* 0.053; *2* 0.0329; *3* 0.0282; *4* 0.0235; *5* 0.0188; *6* 0.0141; *7* 0.0118

Fig. 3

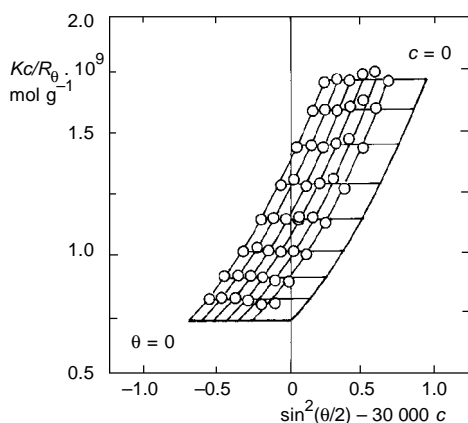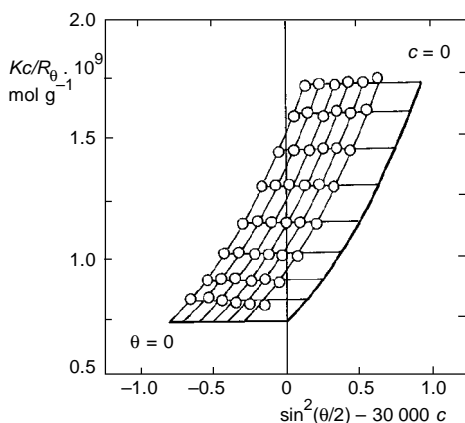Zimm plot for polystyrene latex PS-2 in 4% aqueous acrylamide; c in g ml^{-1}

Fig. 4

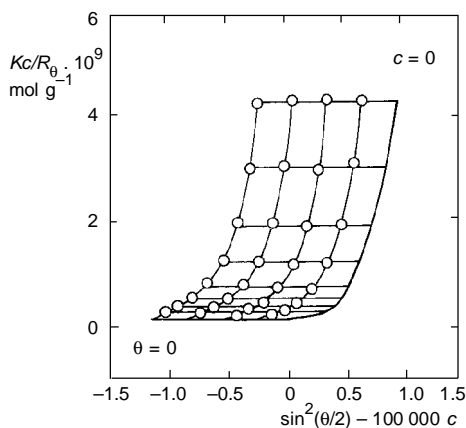Zimm plot for polystyrene latex PS-2 embedded in polyacrylamide gel; c in g ml^{-1}

Fig. 5

Zimm plot for polystyrene latex PS-3 embedded in polyacrylamide gel; c in g ml^{-1}

obtaining molar mass and the radius of gyration is impossible. If we combine, however, the Zimm plotting technique with the Guinier relation using Eqs (4) and (5), we can still extract useful information from the light scattering experiments. Figure 6 shows the ln (Kc/R_θ) plot for the same polystyrene latex embedded in the hydrogel. From the intercept, we obtained molar mass of particles, and from the initial slope we obtained their radius of gyration. We have found again that both molar mass and radius of gyration essentially remain the same during the gelation. For all our latex samples the ratio of radius of gyration to hydrodynamic radius r_g/r_h is between 0.68 and 0.78, close to 0.775, the theoretical value for homogeneous spherical particles. We have compared the molar masses obtained from light scattering experiments with molar masses calculated from the hydrodynamic radius assuming unswollen homogeneous spherical particles:

$$M = 4\pi N_A r_h^3 \rho/3 \ , \tag{6}$$

where ρ is the bulk density of polystyrene. They are essentially the same (Table I). We therefore conclude that polystyrene latexes behave as compact spherical particles both when dispersed in liquid or embedded in PAM hydrogel.

For block copolymer micelles, we have found that the molar mass observed remained unchanged during the gelation process (Fig. 7). Their size, however, decreases after
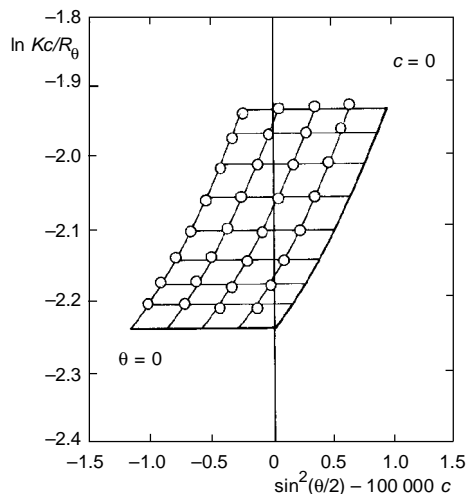

FIG. 6

Plot of ln (Kc/R_θ) vs $kc + \sin^2 (\theta/2)$ for polystyrene latex PS-3 embedded in polyacrylamide gel; c in g ml^{-1}
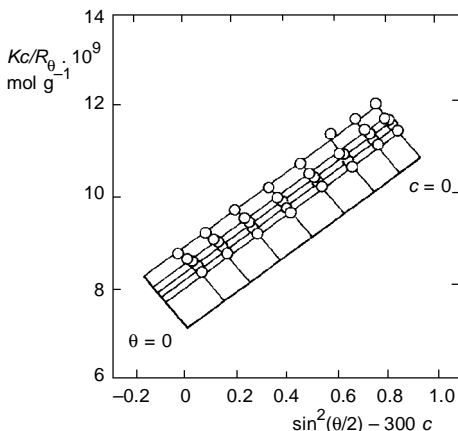
FIG. 7

Zimm plot for copolymer micelles SA-24 embedded in polyacrylamide gel; c in g ml^{-1}

embedding in the soft gel, possibly due to the collapse of poly(methacrylic acid) shells, resulting from their incompatibility with PAM gel. We plan further research in this area.

When we evaluated the light scattering experiments without correcting for turbidity, we obtained in all cases virial coefficients $A_2 \cong 3 \cdot 10^{-6}$ mol cm^3 g^{-2}. While this is a very small value, it is still much larger than the value expected for compact spheres obeying the excluded volume theory. For them, the product A_2M is expected to be of the order of 0.1 or even less[8]. Molar mass of latexes is of the order 10^7 to 10^9 g mol^{-1}. Thus A_2 is expected to be of the order of 10^{-8} to 10^{-10} mol cm^3 g^{-2}. Applying the turbidity correction, we obtained values of A_2 close to zero with an uncertainty about $\pm 3 \cdot 10^{-7}$ mol cm^3 g^{-2}. Thus, it is obvious that the turbidity plays a dominant role in determining the concentration dependence of light scattering in systems with large turbidity and low values of A_2. In this type of experiments, the second virial coefficient is of the order of experimental error and cannot be measured with confidence. Nevertheless, the behaviour of the latex and micelle particles was essentially the same whether in solution or embedded in the gel.

CONCLUSIONS

Light scattering provides useful information about particles embedded in soft hydrogels. For polystyrene latexes, both molar mass and radius of gyration are unchanged before and after embedding in the hydrogel; for block copolymer micelles, molar mass does not change, while the size decreases during gelation, indicating that no particle aggregation takes place and only micellar shells shrink. The magnitude of the fluctuations of particle concentration is not influenced by the presence of the PAM network. In all cases, the second virial coefficient is very small and overshadowed by the turbidity of the sample. For large particles with a narrow distribution of particle sizes, a combination of Guinier and Zimm plots was used for obtaining the particle size and molar mass.

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