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Light Scattering from Coloured Systems: An Example of Polyaniline Dispersions

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SUMMARY: Static light scattering of highly diluted dispersions in 0.005 M H_2SO_4 was used to determine particle parameters of polyaniline dispersions stabilized with colloidal silica. The refractive index of polyaniline n = 1.8 and the refractive index increment (dn/dc) = 0.22 $cm^3 g^{-1}$ at $\lambda = 532$ nm were determined. The light scattering data are affected by the absorption of the green polyaniline and by a small amount of aggregates. The absorption has a negligible effect on the results. The influence of the aggregates was corrected by using the intensity-weighed size distributions determined by dynamic light scattering at different angles and by the two-component separation in static light scattering. Both procedures yield the same result.

Introduction

Polyaniline is one of the most important electrically conducting polymers. Processing of polyaniline, especially in its conducting green emeraldine form, is difficult because of the insolubility in the most solvents. The preparation and application of colloidal polyaniline dispersions may thus be helpful. When aniline is oxidized in the presence of a suitable steric stabilizer, e.g. colloidal silica, dispersions of the polymer are obtained. These are composed of particles in the 300–500 nm diameter range[1]. In an earlier presentation, the course of dispersion polymerization of aniline and the formation of dispersion particles was monitored by dynamic light scattering[2,3]. Additional information on molar mass and other particle parameters can be obtained by static light scattering[4-6]. Colloidal polyaniline particles in their conducting form are well suited as an example for the light scattering study of absorbing particles. Because of the size of the particles and their absorption, the Mie theory[7] should be considered for the evaluation of light scattering data and the applicability of Rayleigh–Debye approximation has to be checked. In high diluted systems thermal lensing, coining of the beam or convection[8] have no influence on the scattering data.

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Light scattering from absorbing dispersions

In absorbing polymer dispersions, the loss of energy abstracted from the incident beam is affected both by light scattering and by absorption of light within the colloidal particles. Therefore, the total intensity of a beam of unit intensity or the extinction cross section, C_{ext}, is the sum of the scattering cross section, C_{sca}, and the absorption cross section[9)], C_{abs}. The corresponding efficiency factors Q are the ratios of the cross sections to the geometric cross section, πr^2, where r is the geometric radius of the particle. The efficiency factors depend on the relative complex index of refraction m and on the size parameter, $x = 2\pi r n_S/\lambda_0$, where λ_0 is the wavelength of light *in vacuo* and n_S the refractive index of the solvent. The relative complex refractive index, $m = m_P/m_S$, is the ratio of the complex refractive index of the particle, $m_P = n_P + ik_P$, and that of the surrounding medium, $m_S = n_S$. In the case of a mixture of two polymer components A and B constituting a particle, the real part of the complex refractive index of the particle, n_P, is the weighed sum $n_P = w_A n_A + (1-w_A)n_B$[10)].

Determination of particle parameters by Rayleigh–Debye approximation

For particles smaller than the wavelength of incident light, $r \ll \lambda_0$, in the framework of the Rayleigh–Debye approximation, the weight-average molar mass M_w of the particles can be determined as

$$\frac{\mathrm{K}c}{R_\theta} = \frac{1}{\mathrm{P}(\theta)}\left(\frac{1}{M_w}\right) \tag{1}$$

with $\mathrm{K} = (4\pi n^2(\mathrm{d}n/\mathrm{d}c)^2)/(\mathrm{N_A}\lambda_0^4)$ being the 'contrast factor' for vertically polarized light of the wavelength λ_0, c the mass concentration of the dispersion, R_θ the Rayleigh ratio, $\mathrm{N_A}$ the Avogadro constant and $\mathrm{d}n/\mathrm{d}c$ the refractive index increment of the dialyzed dispersion. The form factor $\mathrm{P}(\theta)$ is described by Rayleigh's hard-sphere model[11)]

$$P(\theta) = [(\frac{3}{X^3})\ (\sin X - X\cos X)]^2 \tag{2}$$

where $X = (5/3)^{1/2}(4\pi n_s/\lambda_0)R_G \sin(\theta/2)$ and R_G is z-average radius of gyration. This equation fits well the reduced scattering intensity $\mathrm{K}c/R_\theta$ data for each individual concentration. The parameters $1/M_w(c)$ and $R_G^2(c)$ obtained after extrapolation to zero angle were then linearly extrapolated to $c = 0$.

Absorption. In the case of absorbing dispersion particles, the measured reduced scattering intensity $(\mathrm{K}c/R_\theta)_{\mathrm{abs}}$ can be corrected according to

$$\frac{\mathrm{K}c}{R_\theta} = \left(\frac{\mathrm{K}c}{R_\theta}\right)_{\mathrm{abs}} \mathrm{e}^{-\alpha D} \tag{3}$$

with D being the thickness of the cell and α the absorption coefficient of the dispersion particles at $\lambda_0 = 532$ nm at different concentrations, which is obtained from optical spectra.

Aggregated particles

In the dispersions some small aggregated particles occured, which cannot be separated without destroying the dispersion particles. Especially at small angles, the aggregated particles scatter strongly and the determination of M_w of the individual particles is problematic. The contribution of the aggregates to the total intensity of the scattered light, represented by their peak area in the size distribution function was subtracted[12,13)]. The intensity-weighed size distribution at different angles for each concentration can be calculated from the intensity autocorrelation function determined by dynamic light scattering.

Experimental

Preparation of polyaniline dispersions. Aniline hydrochloride (2 mmol) was dissolved in 6.8 ml of destilled water and 1 ml of colloidal silica (40 wt. % SiO_2 aqueous suspension Ludox AS-40; Aldrich) was added. The solution was thermostated to 0° C and 2 ml of 1M aqueous solution of ammonium peroxydisulfate (= 2 mmol) of the same temperature was added to start the polymerization. The mixture was briefly stirred and then kept at rest during the following reaction. The resulting dispersion was dialyzed against water to remove low-molecular-weight components. Conversion to polyaniline and the factor of dilution by the dialysis were determined by optical spectroscopy. For defined protonation of polyaniline, the following investigations were done after dilution with 0.005 M H_2SO_4. The spectra of the diluted dispersions were recorded with a UV-VIS-NIR spectrometer Lambda 19 (Perkin Elmer, USA). The absorption coefficient, α, of polyaniline was calculated from the optical transmission, $t_\lambda = t_0 \exp(-\alpha D)$. The parameter t_0 is the experimental transmission coefficient of all components of the reaction mixture.

Light scattering measurements were carried out at (25.00 ± 0.02)°C by DLS-SLS-5000 Laser Light Scattering Spectrometer/Goniometer (ALV Langen, Germany) equipped with a Nd:YAG laser DPY 315 II (λ_0 = 532 nm, ADLAS, Lübeck, Germany) and a Multiple Tau Correlator ALV-5000. The refractive index increment dn/dc was determined with the differential refractometer DR-1 (ALV Langen, Germany) at 25.0°C and λ_0 = 532 nm.

Results and discussion

Estimation of the refractive index. The refractive index of polyaniline n_{Pani} was estimated by using differential refractometry. The dialyzed polyaniline dispersion contains the particles composed of PANI and colloidal silica and residual free silica. The refractive index increment dn/dc of the dispersion can be approximated as the weighed sum of the constituent parts, $\mathrm{d}n/\mathrm{d}c = w_{\text{Pani}}(\mathrm{d}n/\mathrm{d}c)_{\text{Pani}} + (1-w_{\text{Pani}})(\mathrm{d}n/\mathrm{d}c)_{\text{silica}}$. The increments of polyaniline dispersion in 0.005 M H_2SO_4, $\mathrm{d}n/\mathrm{d}c = 0.111\,\mathrm{cm^3 g^{-1}}$, and that of pure colloidal silica, $(\mathrm{d}n/\mathrm{d}c)_{\text{silica}} = 0.074\ \mathrm{cm^3 g^{-1}}$, were determined experimentally and $(\mathrm{d}n/\mathrm{d}c)_{\text{Pani}} = 0.22\ \mathrm{cm^3\ g^{-1}}$ was calculated. Then the refractive index n_{Pani} =1.80 is estimated from the Lorentz-Lorenz equation[14)] according to

$$\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)_{\text{Pani}} = \frac{(n_{\text{Pani}}^2 - n_{\text{S}}^2)(n_{\text{S}}^2 + 1)}{2\,d\,n_{\text{S}}\,(n_{\text{Pani}}^2 + 2)} \tag{4}$$

where d = 1.35 g cm^{-3} is the density of protonated polyaniline[15)] and n_{S} the refractive index of the solution. As described, the refractive index of the dispersion particles, n_{P} = 1.56, is the weighed sum of the components with n_{silica} = 1.46 [16)].

The absorption index $k' = \alpha\lambda/4\pi$ of pure polyaniline was determined by optical spectroscopy from the absorption coefficient α of a film at λ_0 = 532 nm on a glass substrate. In the dispersion particle, the absorption index is $k = w_{\text{Pani}}\, k' = 0.07$, taking into account that the particle is a mixture of the polymer and silica; and silica does not absorb at λ_0 = 532 nm. The relative complex refractive index of the dispersion is m = 1.16 + 0.013 i with n_{S} = 1.3345 for 0.005 M H_2SO_4.

Influence of absorption in Mie theory. For the estimation of the influence of absorption, scattering efficiencies for m = 1.16 + 0.013 i and m = 1.16 with no absorption *vs.* the size parameter were calculated using the program of Barber and Hill[17)] (Fig.1).

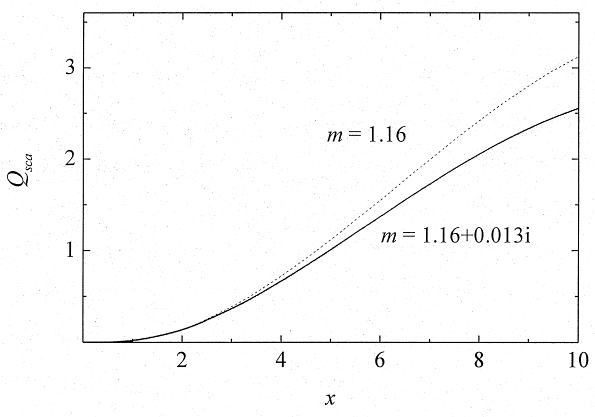

Fig. 1: Scattering efficiency factors Q_{sca} and their dependence on size parameter x

The size parameter $x = 2.7$ is obtained for the hydrodynamic radius $R_H = 172$ nm (see below). For this value the deviation of the two curves is less then 5 % and the absorption index k is negligible.

Influence of particle diameter. The particle diameter is of the same order as the wavelength of the incident light. Not only the size but also the relative refractive index is decisive for the applicability of Rayleigh–Debye approximation. Glatter *et al.* 12) studied the scattering behaviour of colloidal particles by the variation of the size parameter x and the refractive index n. Using their results we conclude that for $n = 1.16$ and in the size range of the particles under investigation, $R_{\mathrm{H}} = 172$ nm, the Rayleigh–Debye approximation can be used for the analysis of light scattering data. Dautzenberg *et al.* 18) showed for particles with $R_G < 500$ nm and $n = 1.159$ the error is smaller than 10 % when using the Rayleigh–Debye approximation instead of the exact Mie treatment. We are well below this limit. From the estimation of the influence of both the absorption and the size of the dispersion particles we are able to conclude, that for data evaluation in the case of silica stabilized polyaniline dispersions the use of Rayleigh–Debye approximation is appropriate.

Corrections of $\mathrm{K}c/R_\theta$. The scattering measurements were carried out at $\lambda_0 = 532$ nm, i.e. in the absorption minimum (Fig. 2a). The absorption coefficients at different concentrations c were recorded (Fig. 2b) and the scattering data were corrected according to equation (3).

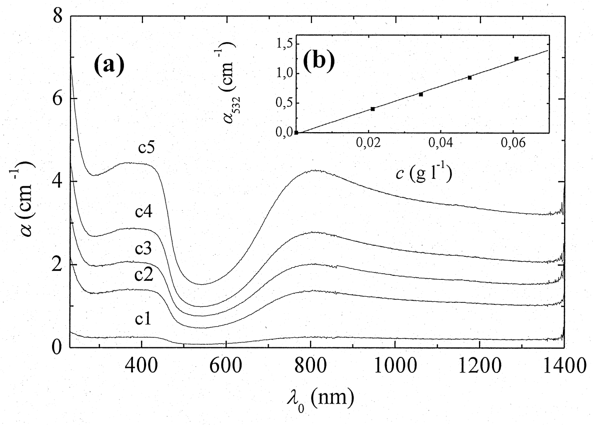

Fig. 2: (a) Optical spectra of polyaniline dispersions for various concentrations of colloidal particles, *c* (see Fig. 2b); (b) the concentration dependence of the absorption coefficient, α (*c*), at $\lambda_0 = 532$ nm

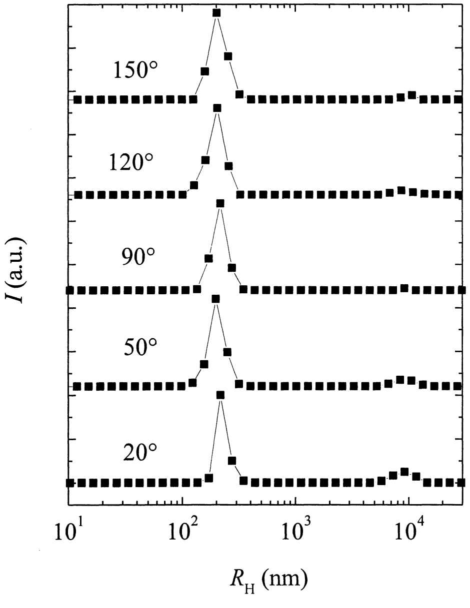

Fig. 3: Intensity-weighed size distribution for $c = 1.166\times10^{-2}$ g l^{-1} recorded at different angles. The curves were arbitrarily shifted for better resolution.

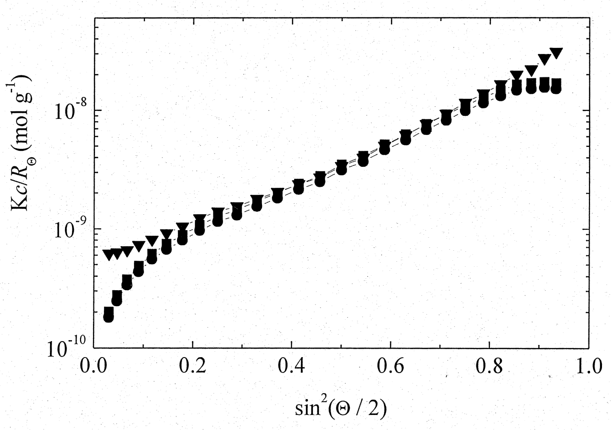

Fig. 4: Light scattering data (■) recorded at different angles for polyaniline dispersions ($c = 1.166\times10^{-2}$ g l^{-1}) after correction for optical absorption (●) and for the aggregation (▼).

The intensity-weighed size distributions recorded at different angles for each concentration were determined by dynamic light scattering. The results for five selected angles are given for $c = 1.166\times10^{-2}$ g l^{-1} in Fig. 3. The peak areas were determined by numerical integration and their ratios used for the correction of the intensity as described above. As expected for monodisperse spheres, no angular dependence of the hydrodynamic radius was found.

The data Kc/R_Θ for all concentrations were corrected for optical absorption and aggregates, as described above. The effect of the corrections for one of the concentrations is shown in Fig. 4. The experimental data were separated into two components $M_w = w_1 M_{w,1} + w_2 M_{w,2}$ by a fit procedure[19,20)] modified for spherical particles[5,21)]. Both components were assumed to be monodisperse spheres. The first component represents the dispersion particles and the second component ($w_2<0.1$) was considered to be aggregates and was not further taken into account for the calculations of M_w. For each concentration $M_{w,app}$ was determined at angle 0°. The results for $1/M_{w,app}$ were plotted *vs.* concentration in Fig. 5 and then linearly extrapolated to $c = 0$.

The data corrected for the absorption were fitted in the same manner and also plotted in Fig. 5. Both linear fits gave the same $M_w = (2.2 \pm 0.1) \cdot 10^9$ g mol^{-1} at $c = 0$. This is a further evidence for the justification of the absorption correction and to neglect absorption in the Mie theory.

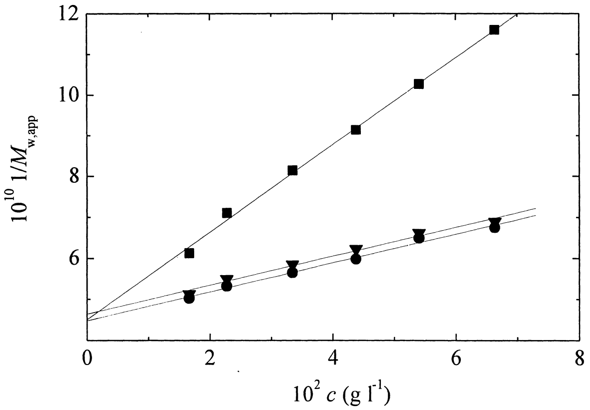

Fig. 5: $M_{w,app}$ obtained from the experimental light scattering data (■) after correction for optical absorption (●) and for the aggregation of particles by two-component separation (▼).

The data obtained after aggregation correction using dynamic light scattering data fits well for a single monodisperse component of $M_w = (2.3 \pm 0.1) \cdot 10^9$ g mol^{-1} and $R_G = 100$ nm. Both the ways, the two-component separation of the static data before the aggregation correction and after its application yielded independently the same result. The ratio $\rho = R_G / R_H$ provides additional information on the structure of the particle[22]. The value $\rho = 0.58$ found for the dispersion particle is lower than 0.775 expected for hard spheres, because the solvent drains the outer shell and cannot deeply penetrate into the particle. The polyaniline particles stabilized with silica have a compact core[2] and the density decreases radially. Similar values were found for microgels[22].

Conclusions

Both static and dynamic light scattering were used to analyse coloured polyaniline dispersions. The absorption of polyaniline does not affect the results of static light scattering and Rayleigh–Debye approximation can be used instead of the exact Mie treatment. The influence of aggregates was eliminated by two-component separation in static light scattering and by the correction of scattering intensities using dynamic light scattering. Both the ways yielded independently the same result, the weight average of the mass of the dispersion particles $M_w = (2.3 \pm 0.1) \cdot 10^9$ g mol^{-1}.

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References

1. J. Stejskal, P. Kratochvil, S.P. Armes, S.F. Lascelles, A.Riede, A., M. Helmstedt, J. Prokeš, I. Křivka, *Macromolecules* **29**, 6814 (1996)
2. A. Riede, M. Helmstedt, V. Riede, J. Stejskal, *Colloid Polym.Sci.* **275**, 814 (1997)
3. A. Riede, M. Helmstedt, V. Riede, J. Stejskal, *Langmuir* **14**, 6767 (1998)
4. J. Stejskal, P. Kratochvíl, P. Koubík, Z. Tuzar, J. Urban, M. Helmstedt, A. D. Jenkins, *Polymer* **31**, 1816 (1990)
5. M. Helmstedt,H. Schäfer, *Polymer* **35**, 3377 (1994)
6. B. Hirzinger, M. Helmstedt, J. Stejskal, *Polymer* **41**, 2883 (2000)
7. G. Mie, *Ann. Phys.* **25**, 377 (1908)
8. A. Sehgal, T.A.P. Seery, Macromolecules **23**, 7807 (1999)
9. M. Kerker, *The scattering of light and other magnetic radiation,* Academic Press, New York 1969, p.49
10. U. Woggon, *Optical Properties of Semiconductor Quantum Dots*, Springer, Berlin 1997, p.103
11. J.W. Rayleigh, *Proc. Roy. Soc. A* **90**, 219 (1914)
12. O. Glatter, M. Hofer, C. Jorde, W.-D. Eigner, *J. Colloid. Interf. Sci.* **105**, 577 (1985)
13. R. Pecora, in: *Measurement of suspended particles by quasi-elastic light scattering*, Dahnke, B.E. (Ed.), J. Wiley & Sons, New York 1983, p. 4
14. J.W. Lorimer, *Polymer* **13**, 46 (1972)
15. B. Lesiak, A. Jablonski, J. Zemek, M. Trchová, J. Stejskal, *Langmuir* **16**, 1415 (2000)
16. H.R. Philipp, in: *Handbook of Optical Constants of Solids*, E.D. Palik (Ed.), Academic Press, San Diego 1991, p. 749
17. P.W. Barber, S.C. Hill, *Light Scattering by Particles: Computational Methods,* World Scientific, London 1990, p.187
18. H. Dautzenberg, M. Hartmann, H. Koch, *Acta Polym.* **30**, 290 (1979)
19. K. Wallenfels, H. Sund, W. Burchard, W. *Biochem. Z.* **335**, 315 (1962)
20. F. Francuskiewicz, H. Dautzenberg, *Eur. Polym. J.* **21**, 455 (1985)
21. M. Helmstedt, J. Stejskal, *Int. J. Polym. Anal. Charact.* **4**, 219 (1997)
22. W. Burchard, in: *Light Scattering, Principles and Development*, W. Brown (Ed.), Clarendon Press, Oxford 1996, p.439