# Simultaneous Frequency-Integrated and Incoherent-Elastic Light Scattering: Description of a New Photon-Correlation Spectrometer

## E. NORDMEIER\* and M. D. LECHNER

Department of Physical Chemistry, University of Osnabrück, 4500 Osnabrück, FRG

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ABSTRACT: A new photon correlation spectrometer has been constructed, that allows the simultaneous recording of frequency-integrated and incoherent-elastic light scattering (FILS and IELS). Its utility and capability are demonstrated in measurements on dilute toluene solutions of narrow-distribution polystyrene as well as on aqueous suspensions of polystyrene–latex particles and their mixtures.  $M_n$  and  $M_w$  values, determined using IELS, are in good agreement with both manufacturers and FILS data. The first reduced cumulant,  $\overline{\Gamma}/q^2$ , shows no angular dependence in the range of 40 to 120°. At smaller and larger angles a drop of  $\overline{\Gamma}/q^2$  is observed, caused by back-scattering and dust-particles. Measurements on mixtures of PS-Latex demonstrate that our spectrometer is capable for detecting the bimodal distribution of spherical particles.

KEY WORDS Light Scattering / Polystyrene / Polystyrene-Latex /

Frequency-integrated and incoherent-elastic light scattering, in the following denoted as FILS and IELS, respectively, are powerful techniques for the characterization of polymers. FILS delivers the mass-average molar mass  $M_w$ , the mean square radius of gyration  $\langle S^2 \rangle_z$  and the second virial coefficient  $A_2$ . IELS-measurements give the diffusion coefficient  $D_r$ , the corresponding hydrodynamic radius  $\langle R_{\rm h} \rangle_z$  and the coefficient  $k_{\rm D}$  of the concentration dependence of  $D_z$ . In some cases, where the molecules have dimensions in the order of the wavelength of the incident light, information about the shape and the architecture of the molecules can be gathered from the angular dependence of the particle scattering factor  $P(q)_z$ , derived by FILS, and the reduced first cumulant  $\overline{\Gamma}(q)/q^2$ , estimated by IELS. Here,  $q = (4\pi/\lambda) \cdot \sin(\theta/2)$  is the wavevector, where  $\lambda$  is the wavelength in the solution, and  $\theta$  is the scattering angle. In addition, the data from FILS and IELS can be combined in various ways,<sup>1</sup> and quite interesting information on molecular structure and polydispersity can be obtained by such combination. For instance, the ratio  $p = \langle S^2 \rangle_z^{0.5} / \langle R_h \rangle_z$  is a significant parameter for the extent of branching and chain rigidity.

During the past decade the parameters from frequency-integrated and incoherent-elastic light scattering have been determined separately using different instruments. In consequence, quantities like p, which are produced by a combination of data from both light scattering techniques, show deviations from each other, caused by systematic errors introduced by different instruments and authors. Errors in the order of twenty or more percent are not unusual. In contradiction, the errors in both techniques are fairly low, 10% for  $\langle S^2 \rangle_z^{0.5}$  and 3% for  $D_z$  or  $\langle R_h \rangle_z$ . Thus, p should be measurable to an accuracy of  $\pm 6\%$ , provided the

<sup>\*</sup> To whom correspondence should be addressed.

systematic errors could be avoided. In principle, this should be possible with a spectrometer, which records both FILS and IELS. On the other hand, a real optimization of such a problem can be achieved only for one quantity of measurement. Here, the mean problem is that, in IELS the scattering volume should be small ( $V \le 0.2 \text{ mm}^3$ ) for a good signal to noise ratio, whereas FILS can be carried out more precisely if the scattering volume is large. Therefore, one had to find a compromise.

## THEORY

# FILS—Background

The light scattering intensity due to optically isotropic polymer coils in dilute solution is governed by the following equation<sup>2</sup>

$$\frac{Kc}{R(c,q)} = \frac{1}{MP(q)} + 2A_2c\cdots$$
 (1)

R(c, q) is the Rayleigh ratio at polymer concentration c (wt/vol) and wave-vector q. K is a constant, which for unpolarized incident light is given by

$$K = 4\pi^2 n_0^2 [(dn/dc)^2/(N_A \lambda_0^4)](1 + \cos^2 \theta) \quad (2)$$

Here,  $n_0$  is the index of refraction of the solvent, dn/dc is the refractive index increment of the solution,  $N_A$  is the Avogadro number,  $\lambda_0$  is the wavelength of the light in vacuum, and  $\theta$  is the scattering angle. The particle scattering factor P(q) can be approximated by  $P(q) = 1 - (q^2 \langle S^2 \rangle_z / 3)$ , when  $q^2 \langle S^2 \rangle_z \ll 1$ .

Then, for a polydisperse sample it holds:

$$\frac{Kc}{R(c,q)} = \frac{1}{M_w} \left( 1 + \frac{q^2 \langle S^2 \rangle_z}{3} \right) + 2A_2 c \qquad (3)$$

Here,  $M_w$  denotes the mass-average mass,  $\langle S^2 \rangle_z$  denotes the z-average square of the radius of gyration, and  $A_2$  represents the second virial coefficient.

# IELS—Study of Polydispersity

The quantity, measured in an incoherentelastic light scattering experiment, is the intensity autocorrelation function of the light scattered at the angle  $\theta$  by the solution of concentration c,

$$g^{(2)}(\tau) = 1 + A |g^{(1)}(\tau)|^2 \tag{4}$$

where  $g^{(1)}(\tau)$  is the electric field autocorrelation function<sup>3</sup> of the scattered light, and A is a constant.  $\tau$  denotes the relaxation time.

The temporal behavior in the scattered light of polydisperse Rayleigh particles may be related to sample diffusive processes. It holds:

$$|g^{(1)}(\tau)| = \int_0^\infty G(\Gamma) \,\mathrm{e}^{-\Gamma \tau} \,\mathrm{d}\Gamma \tag{5}$$

Here,  $G(\Gamma)$  is the distribution of the first cumulant,  $\Gamma = Dq^2$ . D denotes the polymer center-of-mass diffusion coefficient.

The first moment of the distribution  $G(\Gamma)$ ,  $\overline{\Gamma}$ , is given by

$$\bar{\Gamma} = \int_0^\infty \Gamma G(\Gamma) \mathrm{d}\Gamma \tag{6}$$

Expanding  $\exp(-\Gamma\tau)$  about  $\overline{\Gamma}$ ,  $|g^{(1)}(\tau)|$  can be expressed as

$$|g^{(1)}(\tau)| = e^{-\bar{\Gamma}\tau} \left\{ 1 + \frac{\mu_2}{2!} \tau^2 + \frac{\mu_3}{3!} \tau^3 + \cdots \right\}$$

with

$$\mu_n = \langle (\Gamma - \bar{\Gamma})^2 \rangle \tag{7}$$

 $\mu_2$ , for example, is the mean-squared deviation in  $\Gamma$  about  $\overline{\Gamma}$ . Generally, moments beyond  $\mu_2$  are experimentally extremely difficult to determine, as they "buried" in statistical uncertainties in  $g^{(1)}(\tau)$ .

Rearranging eq 7 and using eq 4 one gets:

$$\ln |g^{(2)}(\tau) - 1| = \ln A + 2 \left[ -\bar{\Gamma}\tau + \frac{\mu_2}{2\bar{\Gamma}^2}(\bar{\Gamma}\tau)^2 + \cdots \right]$$
(8)

The moments  $\overline{\Gamma}$ ,  $\mu_2/\overline{\Gamma}^2$  etc. can be calculated by fitting the data of eq 8 by standard least squares procedures. Thereby, the ratio  $\mu_2/\overline{\Gamma}^2$ represents the relative dispersion in the diffusion coefficient about its *z*-average.<sup>4</sup> It holds:

$$\mu_2/\bar{\Gamma}^2 = \langle (D - D_z)^2 \rangle / D_z^2$$
 (9)

with

$$D_{z} = \sum_{i=1}^{N} N_{i} M_{i}^{2} D_{i} \bigg| \sum_{i=1}^{N} N_{i} M_{i}^{2}$$
(10)

where  $M_i$  and  $D_i$  are the mass and diffusion coefficients of polymer molecules of the *i*-th molar mass.

The parameters  $\mu_2/\bar{\Gamma}^2$  and  $D_z$  could be used to estimate the molar masses  $M_n$  and  $M_w$ ,<sup>5</sup> if the relationship between polymer diffusion coefficient and molecular mass was known. Within an experimentally determined molecular mass range, it holds

$$D = C \cdot M^{-\nu} \tag{11}$$

Here, C and v are constants of semiempirical nature. Values of v are in the range  $1/3 \le v \le 1$  with the lower and upper limits for spheres and rods, respectively, and intermediate values for coils, disks, etc.

By substitution of expression 11 into eq 9 and eq 10 one<sup>5</sup> gets

$$D_z = CM_n^{-\nu} [1 + [(2-\nu)(1-\nu)/2]U]/[1+U]$$
(12)

and

$$\mu_2/\bar{\Gamma}^2 = \frac{(\nu^2/4)[U[4+(1-\nu)(\nu-5)U]]}{[1+[(2-\nu)(1-\nu)/2]U]^2} \quad (13)$$

Here,  $U = M_w/M_n - 1$  describes the relative dispersion in the molar mass, in the literature denoted as nonuniformity.

Expressions 12 and 13 reveal some careful consideration. As U grows and at values of v not close to 1,  $\mu_2/\bar{\Gamma}^2$  begins to decrease with increasing U, which is not physically possible. The  $\mu_2/\bar{\Gamma}^2$  versus U curve must have a positive slope; *i.e.*  $\partial(\mu_2/\bar{\Gamma}^2)/\partial U > 0$ . Thus, expressions 12 and 13 can only be used, if

$$(1-v)(7-2v)U < 2$$
 (14)

is fulfilled.

IELS—Study of Binary Polymer Mixtures

The angular dependence of the reduced first cumulant,  $\overline{\Gamma}/q^2$ , of a mixture of particles with different molar masses can be described in the following manner<sup>6</sup>:

$$\bar{\Gamma}/q^{2} = \sum_{i=1}^{N} w(M_{i})M_{i}P_{i}(q)D_{i} / \sum_{i=1}^{N} w(M_{i})M_{i}P_{i}(q)$$
(15)

Here,  $D_i$  is the diffusion coefficient,  $M_i$  is the molar mass,  $w(M_i)$  is the mass fraction, and  $P_i(q)$  is the particle scattering factor of the *i*-th particle.

For a bimodal sized distribution one may write explicitly

$$\bar{\Gamma}/q^2 = \bar{P}_1(q)D_1 + \bar{P}_2(q)D_2$$
 (16)

with

$$\bar{P}_{i}(q) = \frac{w(M_{i})M_{i}P_{i}(q)}{w(M_{1})M_{1}P_{1}(q) + w(M_{2})M_{2}P_{2}(q)}$$
  
 $i = 1, 2 \text{ and } \bar{P}_{1}(q) + \bar{P}_{2}(q) = 1$ 

 $w(M_i)$  and  $M_i$  are known. The particle scattering factors  $P_i(q)$  and the diffusion coefficients can be obtained by separate measurements. Then,  $w(M_i)$ ,  $M_i$ ,  $D_i$ , and  $P_i(q)$  can be compared with the experiment.

#### Combined FILS and EILS

The diffusion coefficient in dilute solutions depends on concentration according to equation

$$D_z = D_{z,0} (1 + k_{\rm D} c + \cdots)^7 \tag{17}$$

where  $k_D = 2A_2M_w - k_f - \bar{v}$ . Here,  $D_{z,0}$  is the center-of-mass diffusion coefficient at infinite dilution. The partial specific volume,  $\bar{v}$ , of the polymer in solution is in the order of one and by orders of magnitude smaller than  $2A_2M_w$ ; it can be neglected in most cases.

 $k_f$  governs the concentration dependence of the molecular friction coefficient

$$f = f_0(1 + k_f c + \cdots)$$
 (18)

It holds  $k_f = k_{f,0} (N_A V_h / M_w)$ ,<sup>8</sup> where  $k_{f,0}$  is the

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frictional coefficient at theta conditions, and  $V_{\rm h}$  is the hydrodynamic volume. There are various theories on the value of  $k_{f,0}$ . For instance, Pyun and Fixman<sup>8</sup> find  $k_{f,0} = 7.16$  for the hard sphere and  $k_{f,0} = 2.23$  for the soft sphere.

The parameters  $D_{z,0}$  and  $f_0$  are connected by the Einstein equation

$$D_{z,0} = k T / f_0$$
 (19)

where k is the Boltzmann constant, and T is the absolute temperature. Additionally, the hydrodynamic radius of coils,  $R_h$ , is related to  $f_0$  by the Stokes equation

$$f_0 = 6\pi\eta R_{\rm h} \tag{20}$$

To a first approximation, polymer chains in good solvents behave both hydrodynamically and thermodynamically like inpenetrable spheres. Then, is holds

$$A_2 = 4N_A \frac{V_h}{M_w^2}^9$$
 (21)

Thus, with  $V_{\rm h} = 4/3 \pi R_{\rm T}^3$  one gets the thermodynamic radius

$$R_{\rm T} = 4.63 \times 10^{-9} (A_2 \cdot M_w^2)^{0.333}$$
(22)

For monodisperse spheres, the radii  $R_h$  and  $R_T$ are identical and larger than the radius of gyration  $\langle S \rangle_z$  by a factor of  $(5/3)^{0.5}$ . For sufficiently long flexible chains in good solvents these radii are expected to differ from one another but to vary with molar mass in the same manner. According to the theory<sup>10</sup>  $R_h$ ,  $R_T$ ,  $\langle S \rangle \langle S \rangle_z \sim M^{0.59}$ .

At last, the dimensionless quantity  $p = \langle S^2 \rangle_z^{0.5} / \langle R_h \rangle_z$  is of interest, which does not depend on the bond length and the degree of polymerization but is a function of the branching density, of polydispersity and of the inherent flexibility of the polymer. For linear chains in good solvents one has p = 1.56, and for monodisperse hard spheres of constant density it holds p = 0.775.<sup>11</sup>

## **EXPERIMENTAL**

Apparatus

A Spectra—Physics He-Ne laser (Model 107S/207;  $\lambda_0 = 633$  nm) is used as light source. The sample cell is a precision bore fused silica tube (8 mm i.d., 10 mm o.d., 8 cm l.) maintained in a toluene refractive index matching bath. The temperature was controlled to within  $\pm 0.01^{\circ}$ C. The scattering angle can be changed in the range of 10 to 140°. The angular accuracy is better than 1 min of arc.

# Correlator

The ALV-3000 Digital Structurator/ Correlator is designed by the ALV Laser Vertriebsgesellschaft (Langen, FRG). Compared to traditional "photon correlators," the following modifications have been introduced to improve measurement accuracy: (1) input count rates up to 100 MHz, sample times down to 40 ns; (2) full preprocessor with random scaler and subtractor; (3) 32 K sample data buffers for real-time and batch procession; (4) linear tau spacing with up to 1024 channels plus optional delay; (5) control of sample temperature in  $0.02^{\circ}$ C steps; (6) setting the scattering angle with 1/100th of a degree precision; and (7) display of laser beam position and pointing stability.

## Data Handling

An analysis of autocorrelation spectra using the method of cumulants can be made particularly simple. The first step is to determine the value of the correlation function at very large delay times. Then, the baseline is obtained by taking the average value of the last 10 channels. After subtracting the baseline from the raw data, the square root is taken, the amplitude is normalized, and the resulting field correlation function  $q^{(1)}(\tau)$ ,

$$g^{(1)}(\tau) = [(g^{(2)}(\tau) - A)/(g^{(2)}(0) - A)]^{0.5} \quad (23)$$

is fitted. Two different methods were applied.

(1) Monodisperse samples (PS-L1, PS-L2,

and PS-L3) yield straight lines, when the logarithm of the correlation function  $g^{(1)}(\tau)$  is plotted *versus* time. Thus, we get  $D_z$  from a simple cumulant-fit.

(2) Polydisperse samples (PS-1 to PS-5) show a little deviation in the linearity between  $\ln g^{(1)}(\tau)$  and  $\tau$ . Thus in order to get the correct value of  $D_z$ , it is physically more reasonable to fit  $\ln[g^{(1)}(\tau) - g^{(1)}(\infty)] = a + b\tau + c\tau^2$ . Here,  $D_z$  can be calculated by  $D_z = \lim_{a \to 0} -b/q^2$ .

Additionally, it should be noted that a fit of the data to two exponentials with variable amplitudes and time constants was not successful.

#### Samples Preparation

Linear polystyrene samples with molar masses  $1.7 \times 10^4$ ,  $1.0 \times 10^5$ ,  $3.9 \times 10^5$ ,  $6.7 \times 10^5$ , and  $2.2 \times 10^6$  g mol<sup>-1</sup> were purchased from National Bureau of Standards. The PSsamples were dissolved in distilled toluene (Merck) by shaken overnight on a wrist shaker. Sample flasks were acid cleaned and then placed for 1 h in an aceton refluxing flask cleaner, before samples were prepared in them. The solutions were clarified by centrifuging for 2 h at 10000 rpm, followed by gentle suction through a  $0.22 \,\mu m$  unipore filter into a light scattering cell. The sample was then inspected for dust, detected by using a He-Ne laser beam. If more than a few dust particles were observed in field of view, the above described procedure was repeated. The concentration of the PS-samples ranged from  $0.5 \text{ gl}^{-1}$  to  $5 \text{ gl}^{-1}$ . At 20°C and  $\lambda = 633$  nm the refractive index of toluene is given by 1.485, and the refractive index increment dn/dc for PS in toluene is  $0.105 \text{ cm}^3 \text{g}^{-1}$ .

Uniform polystyrene latex particles were obtained from Dow Chemical Co. The catalog diameters are 91, 176, and 481 nm, respectively, and the density is  $1.05 \text{ g cm}^{-3}$ . Dilute latex suspensions were prepared from a stock suspension ( $10 \text{ wt}_{0}^{\circ}$ ). A small amount of latex was diluted with freshly prepared doubledistilled water and filtered through an unipore filter of a  $0.22 \,\mu$ m nominal pore size. The concentration of the latices ranged from approximately  $10^{-4}$  to  $10^{-20}$  solid latex. The exact concentrations were not determined, because the results exhibited no concentration dependence. All light scattering measurements were performed within one week from the dissolution of  $\cdot$  a sample. A separate experiment indicated, that over a period of one month no change took place in either the frequencyintegrated or the incoherent-elastic light scattering properties.

# **RESULTS AND DISCUSSION**

# (A) Polystyrene Standards

In order to prove the reliability of our spectrometer, we study first five well characterized polystyrene standards, dissolved in toluene at 20°C. For a first test, we compare the FILS results with data recorded by a photometer Fica 50 from Sofica. Values of  $M_w$ ,  $A_2$ , and  $\langle S^2 \rangle_z^{0.5}$  are listed in Table I. The agreement between the results, derived by the two spectrometers, is acceptable. Over the full range of molar masses the results for  $A_2$  and  $\langle S^2 \rangle_z^{0.5}$  can be described reasonable well by power laws with an uncertainty in the exponents of  $\pm 0.03$ . It holds:

$$A_2 = 2.2 \times 10^{-2} M_w^{-0.35} \,\mathrm{cm}^3 \,\mathrm{mol} \,\mathrm{g}^{-2}$$
 (24)

$$\langle S^2 \rangle_z^{0.5} = 1.4 \times 10^{-9} M_w^{0.592} \,\mathrm{cm}$$
 (25)

The relationships 24 and 25 agree well with those estimated by Raczek.<sup>12</sup> Additionally the exponent 0.592 is very close to that of 0.588, predicted by theory.<sup>10</sup>

Next, we examine the IELS results. In Figure 1,  $D_z(c) = \lim_{q \to 0} \overline{\Gamma}(q, c)/q^2$  is plotted

against the polymer concentration c. The dependence of  $D_z(c)$  on c is well represented by a straight line, from which  $D_{z,0}$  and  $k_D$  can be estimated. Values of  $D_{z,0}$  and  $k_D$  are summarized in Table II.

#### E. NORDMEIER and M. D. LECHNER

Sample	Spectrometer for simultaneous FILS and IELS			Fica 50		
	A:	$A_2 \times 10^4$	$\langle S^2 \rangle_z^{0.5} \times 10^{-7}$	$M_w \times 10^{-6}$	$\frac{A_2 \times 10^4}{\text{cm}^3 \text{mol}\text{g}^{-2}}$	$\frac{\langle S^2 \rangle_z^{0.5} \times 10^{-7}}{\text{cm}}$
	$M_{w} \times 10^{-6}$	$M_{\rm w} \times 10^{-6}$ $- {\rm cm^3  mol  g^{-2}}$	cm			
PS-1	0.12	3.9	12.8	0.09	4.2	11.5
PS-2	0.44	2.4	29.0	0.38	2.2	25.0
PS-3	0.72	2.0	39.8	0.85	2.1	42.0
PS-4	1.20	1.7	50.6	1.15	1.9	49.5
PS-5	2.55	1.3	80.7	2.40	1.1	76.6

 
 Table I.
 Comparison of FILS results of PS-standards in toluene at 20°C, derived by several instruments



Figure 1. Concentration dependence of the translation diffusion coefficient  $D_z$  of the polystyrene samples in toluene at 20°C.

Table II.IELS-measurements on PS in toluene<br/>at 20°C

		$D_{z,0} \times 10^7$	k <sub>D</sub>	
Sample	$M_w^a \times 10^{-6}$	$\mathrm{cm}^2\mathrm{s}^{-1}$	$\mathrm{cm}^3\mathrm{g}^{-1}$	
<b>PS-</b> 1	0.10	4.69	22.2	
PS-2	0.39	2.06	73.6	
PS-3	0.67	1.50	118.4	
PS-4	1.00	1.17	170.2	
PS-5	2.20	0.73	336.0	

<sup>a</sup> Values estimated by the manufacturer.

The data are well described by power laws:

$$D_{z,0} = 4.80 \times 10^{-4} M_w^{-0.602} \,\mathrm{cm}^2 \,\mathrm{s}^{-1}$$
 (26)

$$k_{\rm D} = 8.84 \times 10^{-4} M_w^{0.880} \,{\rm cm}^3 \,{\rm g}^{-1}$$
 (27)

The agreement with measurements of

Raczek<sup>12</sup> is quite good. For the power law  $D_{z,0} = C \cdot M_w^{-\nu}$ , he got the values  $C = 3.32 \times 10^{-4}$  and  $\nu = 0.574$ . Raczek's data may be a little more acurate than our data, because he used ten PS-standards instead of five. Thus, in order to determine  $M_n$  and  $M_w$  by means of IELS, we use his values.

First, we prove condition 14. It holds  $2.49 \cdot U < 2$ . Thus, expressions 12 and 13 can be used without restriction.

Values of  $M_n$ ,  $M_w$ , and U, estimated by IELS and independently by the manufacturer, are presented in Table III. The IELS results are in good agreement with manufacturers  $M_n$ and  $M_w$  data. Values of U, found by IELS, are significant to small, when  $U \leq 0.20$ . Samples with a polydispersity larger than U=0.20 may be measured, correctly, as expected. A similar result was found by Selser.<sup>5</sup> Finally, we investigate how precisely parameters like p = $\langle S^2 \rangle_z^{0.5} / R_h$ ,  $r = R_T / R_h$ , and  $k_{f,0}$  can be obtained by simultaneous FILS and IELS. Values of p, r, and  $k_{f,0}$  are given in Table IV. They are affected with errors, which are not very small, but which are about fifty or more percent lower than those obtained by using different spectrometers for FILS and IELS.

The ratio p is insensitive to molar mass within the experimental error of 6%. Nevertheless, it seems that p decreases slowly but perceptibly with  $M_w$ ; the hydrodynamic size and the physical size of PS-coils vary with

Sample	IELS			Manufacturer		
	$M_n \times 10^{-6}$	$M_w \times 10^{-6}$	U	$M_n \times 10^{-6}$	$M_w \times 10^{-6}$	U
<b>PS-</b> 1	0.10	0.10	0.00	0.09	0.10	0.11
PS-2	0.38	0.42	0.11	0.33	0.39	0.18
PS-3	0.62	0.68	0.10	0.56	0.67	0.20
PS-4	1.22	1.35	0.11	1.00	1.20	0.20
PS-5	1.62	1.96	0.21	1.80	2.22	0.25

Table III

 Table IV.
 Comparison of experimental and theoretical size ratios

Sample	$M_w \times 10^{-6}$	$\langle S^2 \rangle_z^{0.5} / R_{\rm h}$	$R_{\rm T}/R_{\rm h}$	<i>k</i> <sub>f.0</sub>
PS-1	0.10	1.51	0.86	5.7
PS-2	0.39	1.49	0.79	4.8
PS-3	0.67	1.49	0.77	4.5
PS-4	1.20	1.48	0.75	4.0
PS-5	2.22	1.47	0.72	3.4
Theory		[1.24—1.56]	[0.0—1.02]	[2.23—7.18]
Error		6%	8%	12%

molar mass in slightly different ways. The exponent v obtained for the power law of  $R_h$  (v=0.602) is considerably higher than that one obtained for  $\langle S^2 \rangle_2^{0.5}$ . The average value of p is 1.49, which is in reasonable agreement with that of p=1.56, stated by the theory of self-avoiding coils in good solvents. The ratio r decreases significantly with increasing molar mass. Values of r lie between the theoretical value of 0.0 for unperturbed coils and 1.02 for self-avoiding coils.

Values of  $k_{f,0}$ , calculated from values of  $k_D$ ,  $A_2$ , and  $M_w$  using eq 18, are similarly sensitive to  $M_w$  as r. It holds:  $\partial k_{f,0}/\partial M_w < 0$ . Values found for  $k_{f,0}$  lie between 2.23 and 7.18, predicted by theory for unperturbed coils and spheres. In summary, the above considerations turn out that dimensionless quantities like p, r, and  $k_{f,0}$  are sensitive to molar mass or structure changes, respectively. But it also shows that light scattering experiments alone rarely, if ever, allow a unique determination of structure. For this one depends on additional data from chemical or kinetic experiments.



Figure 2. Angular dependence of the reduced first cumulant for PS-Latex particles of diameters with d = 91 nm, d = 176 nm, and d = 481 nm in water at  $20^{\circ}$ C.

## (B) PS-Latex Particles

For a further check of our spectrometer three PS-Latex samples with particle diameter of 91, 176, and 481 nm were examined in water at 20°C. Figure 2 gives a plot of  $\overline{\Gamma}/q^2$ , derived by a normal cumulant fit, against  $\theta$ . The filled circles denote data of  $\overline{\Gamma}/q^2$ ,  $(D_z^E)$ , which are extrapolated to zero wave-vector. In Table V,  $D_z^T$  denotes the theoretical expected value of

#### E. NORDMEIER and M. D. LECHNER

Sample	Angle	$\frac{\bar{\Gamma}/q^2 \times 10^8}{\mathrm{cm}^2  \mathrm{s}^{-1}}$	$\mu_2$	$\frac{D_Z^{\rm E} \times 10^8}{\rm cm^2  s^{-1}}$	$\frac{D_Z^{\mathrm{T}} \times 10^8}{\mathrm{cm}^2 \mathrm{s}^{-1}}$
	60	4.65	0.02		
PS-L1	80	4.61	0.02	4.63	4.73
[d = 91  nm]	100	4.68	0.03		
	120	4.58	0.05		
	140	4.32	0.12		
	40	2.28	0.04		
	60	2.42	0.03		
PS-L2	80	2.38	0.03	2.39	2.45
[d = 176  nm]	100	2.44	0.04		
	120	2.32	0.08		
	140	2.00	0.18		
	40	0.82	0.04		
	60	0.86	0.02		
PS-L3	80	0.84	0.02	0.85	0.90
[d = 481  nm]	100	0.88	0.02		
-	120	0.75	0.12		
	140	0.32	0.35		

Table V. PS-Latex particles in water at 20°C

the center-of-mass diffusion coefficient, estimated by the manufacturer.  $\mu_2$  is the second cumulant.

First, it should be noticed that the values obtained for  $\bar{\Gamma}/q^2$  don't show any concentration dependence. Thus,  $D_z^E$  is identical with  $D_{z,0}$ . Second, the measured center-of-mass diffusion coefficients  $D_z^E$  coincide with the theoretical expected values of  $D_{z,0}$  within the experimental error of 3-5%. In addition, the results for the Latices PS-L1 and PS-L2 yield hydrodynamic radii of 46.5 or 90.2 nm and radii of gyration of 38.1 or 72.2 nm, leading to ratios p=0.82 or p=0.80, which agree well with the theoretical value of p=0.775 for a hard sphere. Finally, we study the angular dependence of the reduced first cumulant. Theory<sup>13</sup> predicts no angular dependence of  $\overline{\Gamma}/q^2$  for monodisperse hard spheres. Such behaviour is indeed observed for all three PS-Latex samples in the angle region from 40 to  $120^{\circ}$ . At angles outside this range a sudden decrease of  $\overline{\Gamma}/q^2$  is observed. Additionally, at angles larger than 120° an increase of the

second cumulant  $\mu_2$  is found, which originates in an increasing deviation of the autocorrelation function  $g^{(1)}(\tau)$  from a single exponential function. This behaviour might be due to back-scattering, which occurs due to reflection of the primary beam at the solution-glass boundary of the cell or at the glass-air boundary of the index matching bath, however. In fact, such deviations are slightly smaller for samples of PS in toluene, where the refractive index of the solution is much closer to that of the cell or the bath glass than in that of water. On the other hand, at small angles ( $\theta < 40^{\circ}$ ) back-scattering should cause  $\overline{\Gamma}/q^2$  increase as q decreases.<sup>6</sup> However, the opposite is found. Accordingly, the decrease in  $\overline{\Gamma}/q^2$  might be also due to a few dust particles in the solution, which couldn't be removed by clarification.

# (C) Mixtures of PS-Latex Particles

Up to yet, we have demonstrated that our spectrometer works accurately with regard to the determination of FILS and IELS properties of particles of uniform size. In reality,



Figure 3. Angular dependence of the reduced first cumulant of the PS-Latex mixture, composed of 80% [d=91 nm] and 20% [d=176 nm], in water at  $20^{\circ}$ C: •, experiment; —, theory.

frequently either the size distribution or the molar mass distribution is broad. Therefore, it is instructive to examine the performance of our spectrometer in IELS-measurements on a known bimodal mixture of PS-Latex particles. Here, we choose a mixed sample where the mass fractions of one component (d=91 nm) is 80% and 20% for the other component (d=176 nm). Measurements were made at T=20%C in the angular range of 30 to 120%. The data were analysed by using the cumulant and the histogram method.

(1)Cumulant Method. The reduced first cumulants of PS-Latex spheres having diameters 91 and 176 nm were found to be independent on scattering angle over the whole range of 30 to  $120^{\circ}$ . In contrast for the mixture,  $\overline{\Gamma}/q^2$  shows, as seen in Figure 3, a strong nonlinear dependence on  $\theta$ , where the experimental curve is situated between the limits of the diffusion coefficients of the two components. Similar observations were found for samples of different mass ratios of the two components. As outlined in the theoretical section the curvature of  $\overline{\Gamma}/q^2$  can be calculated if the mass fractions, the diffusion coefficients and the particle scattering factors, characterising the single components, are known. Indeed, this is the case. The result of such a calculation is also shown in Figure 3. It turns out that the





Figure 4. Uni- and bimodal  $G(\Gamma)$  distributions. (a) and (b) PS-Latex particles considered as uniform; (a) d = 91 nm and (b) d = 176 nm. (c) PS-Latex mixture with mass fractions of 80% [d = 91 nm] and 20% [d = 176 nm].

theoretical curve agrees very well with the experimental curve. However, when only  $w(M_1)$ ,  $P_1(q)_z$  and  $P_2(q)_z$  are known, a fit for  $D_1$  and  $D_2$  is not better than 10% for  $D_1$  and 30% for  $D_2$ . Also, if  $D_1$ ,  $D_2$ ,  $P_1(q)_z$  and  $P_2(q)_z$  are known and  $w(M_1)$  or  $w(M_2)$  are unknown, a fit for  $w(M_1)$  or  $w(M_2)$  is not better than 20%. These errors are too high to ensure a reliable characterization of a bimodal distribution of PS-Latex particles.

(2) Histogram Method. The histogram method, developed by Chu,<sup>14</sup> delivers the  $\Gamma$  distribution  $G(\Gamma)$ . Here,  $G(\Gamma) d\Gamma$  denotes the fraction of the total integrated intensity of light scattered by the particles which obey  $\Gamma = Dq^2$  within the increment  $d\Gamma$ .  $G(\Gamma)$  can be derived without prior knowledge about the shape of the distribution on the basis of the ALV 3000 algorithmus, developed by Peters.<sup>15</sup> The results are shown in Figure 4, where (a)

and (b) are  $G(\Gamma)$  of the single component and (c) is  $G(\Gamma)$  for the mixture. We clearly see, that (c) is a bimodal distribution, where the two maxima appear at the positions expected from  $\Gamma$  of the single components (a) and (b). Furthermore, the ratio of the integrated scattered intensities calculated from the peak areas for the single components is close to the value  $w(M_1)/w(M_2)$  of their mass fractions. These results point out, that if we use the histogram method, our spectrometer works accurately for detecting the bimodal distribution of PS-Latex spheres.

## CONCLUSIONS

In summary, we can state, that the spectrometer, presented here, allows to carry out simultaneous frequency-integrated and incoherent elastic light scattering measurements with high accuracy. At first sight, this may be surprising, since the conditions for optimization of both techniques are exclusive. However, our results demonstrate excellent agreement with literature values. In fact, instruments designed special for FILS or IELS alone may yield a higher accuracy than can be ever obtained with our spectrometer. Nevertheless, the advantage of simultaneous FILS and IELS is obvious. Acknowledgment. We are grateful to Mr. W. Peters, ALV-Laser Vertriebsgesellschaft, Langen, for the accurate manufacture of the various electronic and mechanical parts of the spectrometer. Financial support of this work by the "Fonds der Chemischen Industrie" is kindly appreciated.

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