Screening and excess low-angle scattering in semidilute solutions of polystyrene in benzene

E. Wendt and J. Springer
Institut für Technische Chemie der Technischen Universität Berlin, Fachgebiet Makromolekulare Chemie, Strasse des 17 Juni 135, 1000 Berlin 12, FRG

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Dilute and semidilute solutions of three high-molar-mass polystyrenes ($1.44 \times 10^6\,\mathrm{g\,mol^{-1}} \leqslant M_w \leqslant 8.45 \times 10^6\,\mathrm{g\,mol^{-1}}$, $0.49\,\mathrm{g\,l^{-1}} \leqslant c \leqslant 24.82\,\mathrm{g\,l^{-1}}$) in benzene have been studied by light scattering ($\lambda_0 = 546\,\mathrm{nm}$, $T = 20°\mathrm{C}$). Independent of molar mass the onset concentration for the excess scattering is $c \sim 4\,\mathrm{g\,l^{-1}}$. The screening length, the molar mass of blobs and the correlation length of long-range heterogeneities were obtained from light scattering curves by a four-parameter model. The concentration dependence of the screening length and the molar mass of blobs are consistent with power laws predicted by the scaling theory. The correlation length of the long-range heterogeneities does not depend on molar mass or concentration. Their mean size was found at 100 nm.

(Keywords: light scattering; scaling theory; polystyrene; semidilute solutions; screening length; long-range heterogeneities)

INTRODUCTION

The thermodynamic properties of polymer solutions and the structure of chain molecules in solution can be investigated by scattering experiments. Depending on the source of primary light these are differentiated into light, neutron and X-ray scattering. In recent times many papers[1-12] have employed scattering experiments of semidilute solutions. It is possible to discuss these data on the basis of the theoretical work of de Gennes[13] and Doi and Edwards[14].

Independent of the source of primary light some authors[9-12,15,16] have reported an anomalous shape of the scattering curves in the case of solutions of polystyrene. One observes a strong rise in scattering intensity at relatively small values of the scattering vector. This scattering is called excess low-angle scattering (ExLAS) or enhanced low-angle scattering (ELAS). According to Koberstein *et al.*[12] this scattering is due to density fluctuations in solution as a consequence of long-range heterogeneities (LRH), whose structure[11,12] is unknown till now. In a previous work[10], we have investigated the small-angle X-ray scattering (SAXS) of semidilute solutions of polystyrene (PS) in benzene. Because the resolution is too small in the range of small values of the scattering vector, we cannot make any comments about concentration or molecular weight dependence of the LRHs. Therefore, it was the purpose of the present work to prove by light scattering on solutions of high-molar-mass PS in benzene whether the ExLAS is dependent on concentration and degree of polymerization.

The excess scattering curves were evaluated according to a four-parameter model given by Koberstein *et al.*[12] Thus quantities were obtained for discussions of de Gennes'[13] scaling relationships for semidilute solutions.

THEORY

The weight-average molar mass M_w, the mean-square radius of gyration $\langle R^2 \rangle$ and the second osmotic virial coefficient A_2 can be calculated from the intensity of scattered light according to the extrapolation method given by Zimm[17]:

$$\frac{Kc}{I(h)} = \frac{1}{M_w} + \frac{1}{M_w} \frac{\langle R^2 \rangle}{3} \frac{16\pi^2}{\lambda^2} \sin^2 \theta + 2A_2 c + \ldots \qquad (1)$$

where K is an optical constant, c the concentration of macromolecules in solution, $I(h)$ the Rayleigh ratio, $h = (4\pi/\lambda)\sin\theta$ the value of the scattering vector, λ the wavelength of incident light in the solution and 2θ the angle between the scattered and incident light.

In the case of random-walk statistics, the mean-square radius of gyration and the molar mass are connected by the power law:

$$\langle R^2 \rangle^{1/2} \propto M^{\nu} \qquad (2)$$

with $\nu = 0.5$. The exponent 0.5 was obtained for PS in a Θ-solvent and in the solid phase[18]. In good solvents, expansion of the macromolecules takes place as a consequence of the excluded volume. In this case according to the theory by Flory[19] the exponent ν in equation (2) is 0.6, which was confirmed by experiments with PS solutions[18].

In dilute solutions the macromolecules are isolated. In this state the volume is $\sim \langle R^2 \rangle^{3/2}$. In more concentrated solutions the macromolecules begin to overlap. The overlap concentration c^* describes the transition from dilute to semidilute solution. According to de Gennes[13],

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Dedicated to Professor Kurt Veberreiter on his 75th birthday

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c^* is defined by:

$$c^* = \frac{M}{N_A \langle R^2 \rangle^{3/2}} \tag{3}$$

where N_A is Avogadro's number. According to this model, the macromolecules in semidilute solutions are regarded as an arrangement of 'blobs'. The single blobs are screened from each other and therefore their mean correlation length is the so-called screening length ξ. The effect of excluded volume does not extend beyond ξ. The overlap concentration is not a sharp limit between dilute and semidilute solutions, but in order to derive the laws for semidilute solutions the definition according to equation (3) is a precondition. In semidilute solutions the screening length is independent of the molar mass of dissolved macromolecules but is a function of their concentration. The dependence is given by:

$$\frac{\xi}{\langle R^2 \rangle^{1/2}} \propto \left(\frac{c}{c^*}\right)^{k_1} \tag{4}$$

with $k_1 = -\nu/(3\nu - 1)$. If one blob contains g polymer segments with molar mass M_g, we can write $M_{\text{blob}} = gM_g$. It follows by analogy with equation (2) that:

$$\xi \propto M_{\text{blob}}^{\nu} \tag{5}$$

The combination of equations (4) and (5) yields the dependence of the blobs' molar mass on concentration:

$$M_{\text{blob}} \propto c^{k_2} \tag{6}$$

with $k_2 = -1/(3\nu - 1)$. If $\nu = 0.6$, then $k_1 = -0.75$ and $k_2 = -1.25$.

According to de Gennes[13] the structure factor of blobs is given by an Ornstein–Zernicke law:

$$G(h)_{\text{blob}} = \frac{1}{1 + \xi^2 h^2} \tag{7a}$$

The structure factor of LRHs defined by Koberstein *et al.*[12] is:

$$G(h)_{\text{LRH}} = \frac{1}{(1 + a^2 h^2)^2} \tag{7b}$$

where a is the mean correlation length of the LRHs.

Taking the structure factor from equation (7a) one gets linear scattering curves in the Zimm plots ($Kc/I(h)$ against h^2). If there is an excess scattering, then the scattering curves will be non-linear in the Zimm plots (see *Figure 2*). The difference from linearity increases with decreasing scattering vector. In this case the scattering intensity can be expressed as a sum of the scattering intensity of blobs $I(h)_{\text{blob}}$ and the excess scattering intensity $I(h)_{\text{LRH}}$:

$$I(h) = I(h)_{\text{blob}} + I(h)_{\text{LRH}} \tag{8}$$

with

$$I(h)_{\text{blob}} = K\phi_1 c M_{\text{blob}} G(h)_{\text{blob}} \tag{9a}$$

and

$$I(h)_{\text{LRH}} = K\phi_2 c M_{\text{LRH}} G(h)_{\text{LRH}} \tag{9b}$$

Here M_{LRH} is the molar mass of the polymer segments within one structure unit of the LRHs; ϕ_1 and ϕ_2 are the mass fractions of polymers in respectively blobs and LRHs. If $\phi_2 \ll 1$, then $\phi_1 \sim 1$. On this assumption, from equations (7), (8) and (9) it follows that:

$$\frac{I(h)}{Kc} = \frac{M_{\text{blob}}}{1 + \xi^2 h^2} + \frac{\phi_2 M_{\text{LRH}}}{(1 + a^2 h^2)^2} \tag{10}$$

To analyse the scattering curves with excess intensity, Koberstein *et al.*[12] drew a straight line in the linear range of the Zimm plots (high h values). This straight line represents the first term in equation (10). The excess intensity is equal to the difference between the measured intensity and the extrapolated straight line. For this purpose $(I(h)_{\text{LRH}})^{1/2}$ against h^2 is evaluated. For the evaluation of our scattering curves with excess intensity, we are going another way. The four parameters of the model (M_{blob}, ξ, $\phi_2 M_{\text{LRH}}$ and a) are calculated by a least-squares fit of the scattering curves (equation (10)) by the program LOREQ1. On the basis of variances, the errors of the parameters are determined. Details will be reported in our next paper[20].

EXPERIMENTAL

The light scattering measurements were performed by a Fica 50 light scattering photometer with vertically polarized primary light ($\lambda_0 = 546$ nm) at $T = 20 \pm 0.5$°C. The bath liquid for the thermoregulation of the cuvette was benzene. The same solvent was used for calibration of the apparatus. The refractive index[21] n_1 for pure solvent (benzene) and the refractive index increment[21] $\mathrm{d}n/\mathrm{d}c$ for solutions of PS in benzene were 1.5052 and $0.103_4\,\mathrm{cm^3\,g^{-1}}$ respectively. The scattering curves were measured in steps of 5° in the angle range between 30° and 150°. Multiple scattering was not taken into consideration. The investigations were carried out with three high-molar-mass PS samples. PS1 and PS2 were purchased from PSS (Polymer Standards Service), Mainz. The polystyrene sample PS3 was anionically prepared in our laboratory[22]. The solvent benzene 'p.A.' (Merck, Darmstadt) was used as received.

In all cases solutions were prepared with weighed polymer samples in volumetric flasks and were shaken for one week for complete mixing. Before measurement, the solutions were filtered through a glass-fibre prefilter (Sartorious, Göttingen) directly into the scattering cells. The scattering cells were cleaned and made free of dust by tetrahydrofuran.

RESULTS AND DISCUSSION

Figures 1–3 show Zimm plots for a measured concentration series of PS2. Up to concentration $c = 2.14\,\mathrm{g\,l^{-1}}$ the curves are linear (*Figure 1*). Above $c = 4.07\,\mathrm{g\,l^{-1}}$ the curves decline in the small h value region (*Figures 2* and *3*). The excess scattering increases at higher concentrations and a decline of the curves is observed at higher h values. In the case of the three highest concentrations measured, the scattering curves no longer have a linear range. Here, the excess scattering is dominant. The scattering curves for the concentration series of the other polystyrene samples are similar.

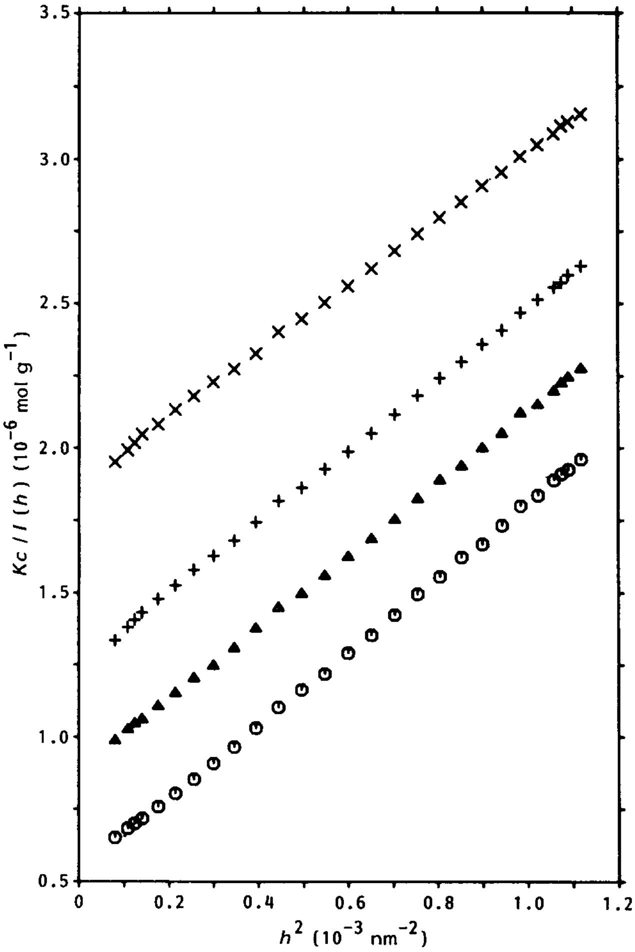

Figure 1 Zimm plots of the light scattering measurements for PS2/benzene: $M_w = 5.65\times10^6\,\mathrm{g\,mol^{-1}}$; (○) $c=0.49$, (△) $c=0.99$, (+) $c=1.48$ and (×) $c=2.14\,\mathrm{g\,l^{-1}}$

independent of molar mass the onset concentration for excess scattering is located at $c\sim4\,\mathrm{g\,l^{-1}}$.

For determination of molar masses and radii of gyrations of the polystyrenes, the scattering curves were evaluated without excess scattering according to equation (1) (for example PS3, *Figure 4*). The results of Zimm extrapolation and the calculated overlap concentrations according to equation (3) are listed in *Table 1*. For M in equation (3) the weight average M_w is used. The data were analysed according to equation (2) even though their number is very small. For the exponent one obtains $\nu=0.58$.

All scattering curves with excess scattering are evaluated with program LOREQ1. The evaluation of scattering curves in *Figure 3* was modified, in a way described later. Generally, all fits agree almost exactly within the range of data (*Figure 5* gives an example). The full curve through the experimental points is calculated according to equation (10). The straight line above the measuring points shows the scattering given by the Ornstein–Zernicke law (first term in equation (10)) and is obtained with program LOREQ1. In opposition to Koberstein *et al.*[12] this curve does not lie at the measuring points even in the range of high h values. This means that the function for excess scattering (second term in equation (10)) will not be zero in the measured range of the scattering vector.

In *Table 2* values are listed for screening length and molar mass of blobs. As expected, both quantities decrease with increasing concentration. The absolute errors of screening length are nearly constant, which means that as a consequence of the decrease of the linear range of scattering curves the relative errors for screening length increase with increasing excess scattering. The absolute errors of M_{blob} decrease with increasing excess scattering, which means that the relative errors are nearly constant. In all cases M_{blob} is the best determined value, the value with smallest errors.

The values for screening length and molar mass of blobs were evaluated according to equations (4), (5) and (6). The least-squares fits are shown in *Figures 6*, *7* and *8*. One obtains the following scaling laws:

$$\frac{\xi}{\langle R^2\rangle^{1/2}} = 0.141\,(\pm0.002)\left(\frac{c}{c^*}\right)^{-0.75(\pm0.04)} \quad (11a)$$

$$\xi = 0.010\,(\pm0.003)(M_{\mathrm{blob}})^{0.59(\pm0.02)} \quad (11b)$$

$$M_{\mathrm{blob}} = 1.50\,(\pm0.02)\,10^6(c)^{-1.27(\pm0.01)} \quad (11c)$$

(for ξ in nm, M_{blob} in $\mathrm{g\,mol^{-1}}$ and c in $\mathrm{g\,l^{-1}}$). The exponents are in excellent agreement with the theory. The result supports the formulation according to equation (10).

The values obtained for the correlation length and quantity $\phi_2 M_{\mathrm{LRH}}$ are given in *Table 3*. Both parameters

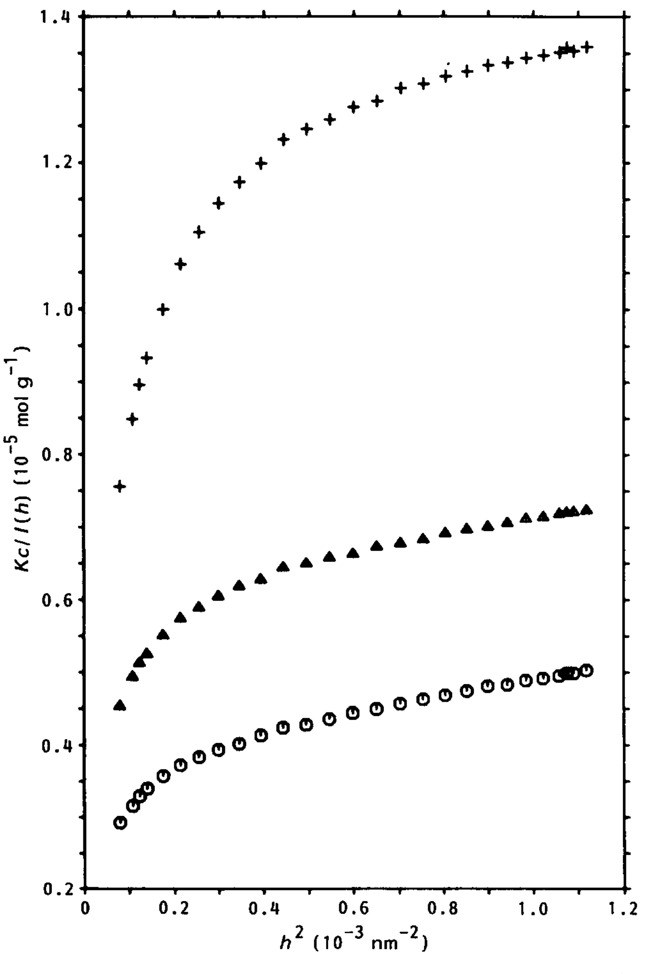

Figure 2 Zimm plots of the light scattering measurements for PS2/benzene: $M_w = 5.65\times10^6\,\mathrm{g\,mol^{-1}}$; (○) $c=4.07$, (△) $c=5.97$ and (+) $c=10.24\,\mathrm{g\,l^{-1}}$

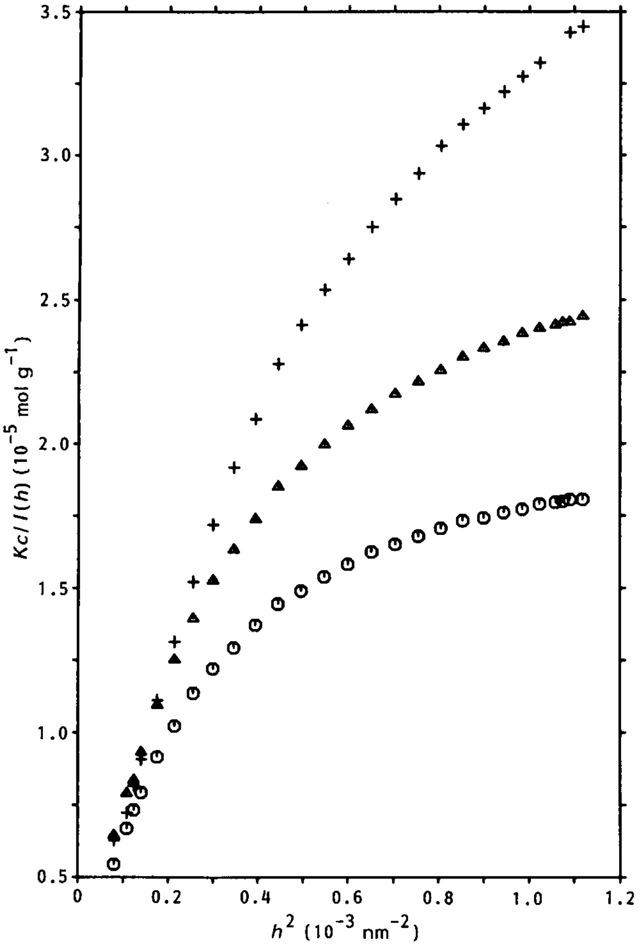

Figure 3 Zimm plots of the light scattering measurements for PS2/benzene: $M_w = 5.65 \times 10^6\,\mathrm{g\,mol^{-1}}$; (○) $c = 14.09$, (△) $c = 17.96$ and (+) $c = 24.82\,\mathrm{g\,l^{-1}}$

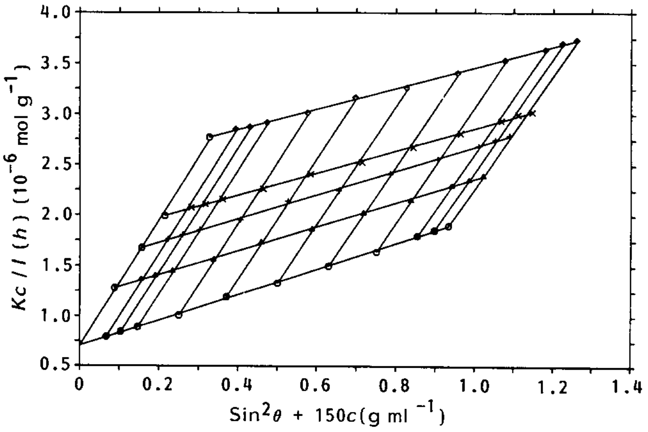

Figure 4 Zimm extrapolation for PS3/benzene: (△) $c = 0.58$, (+) $c = 1.04$, (×) $c = 1.43$ and (◇) $c = 2.18\,\mathrm{g\,l^{-1}}$

Table 1 Results obtained from Zimm extrapolations

Sample	M_w (g mol^{-1})	$\langle R^2\rangle^{1/2}$ (nm)	A_2 (mol cm^3 g^{-2})	c^* (g l^{-1})
PS1	8.45×10^6	194	3.1×10^{-4}	1.94
PS2	5.65×10^6	146	3.5×10^{-4}	3.02
PS3	1.44×10^6	67.8	4.5×10^{-4}	7.65

are affected by high absolute errors, but the errors decrease with increasing concentration and with strong excess scattering respectively. The mean correlation length a of LRHs is probably independent of concentration and molar mass respectively, because the values coincide well within the error of the experiment. The mean value $a \sim 100$ nm is in excellent agreement with the results of Koberstein *et al.*[12] The dependence of concentration of correlation length of LRHs is not

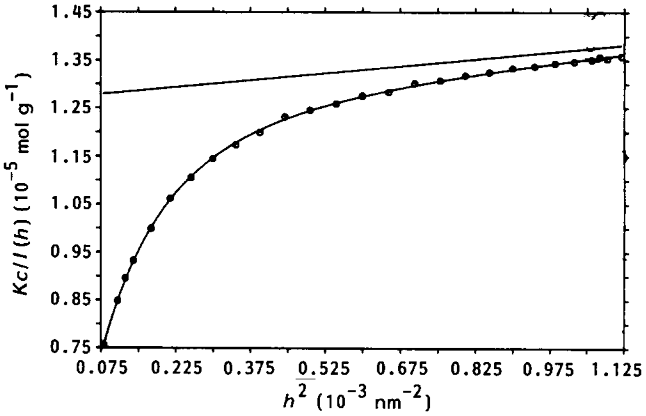

Figure 5 Fit with program LOREQ1 to a measured scattering curve (see text) for PS2/benzene: $M_w = 5.65 \times 10^6\,\mathrm{g\,mol^{-1}}$, $c = 10.24\,\mathrm{g\,l^{-1}}$

Table 2 Screening length ξ and molar mass of blobs M_{blob} evaluated with program LOREQ1

M_w (g mol^{-1})	c (g l^{-1})	ξ (nm)	M_{blob} (g mol^{-1})
8.45×10^6	2.03[a]	26.3 ± 0.4	609 000 ± 6000
	2.98	19.6 ± 1.2	377 000 ± 15 000
	4.00	15.8 ± 0.9	261 000 ± 7000
	5.97	11.1 ± 1.2	156 000 ± 4000
	8.07	10.1 ± 1.0	110 000 ± 2000
	10.11	8.0 ± 1.3	81 800 ± 2000
5.65×10^6	4.07	16.2 ± 0.8	255 000 ± 5000
	5.97	12.4 ± 0.9	160 000 ± 3000
	10.24	8.8 ± 1.2	78 600 ± 2000
1.44×10^6	11.07	6.0 ± 0.9	65 400 ± 2000
	16.04	4.2 ± 1.2	40 700 ± 3000

[a] Without finding excess scattering

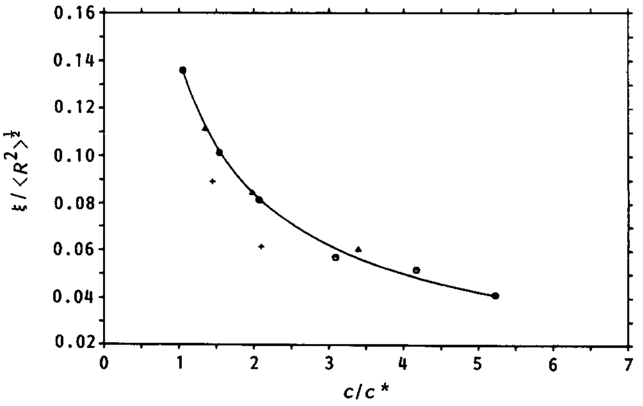

Figure 6 Standardized screening length $\xi/\langle R^2\rangle^{1/2}$ *versus* reduced concentration c/c^*: (○) $M_w = 8.45 \times 10^6$, (△) $M_w = 5.65 \times 10^6$ and (+) $M_w = 1.44 \times 10^6\,\mathrm{g\,mol^{-1}}$ (see *Tables 1* and *2*)

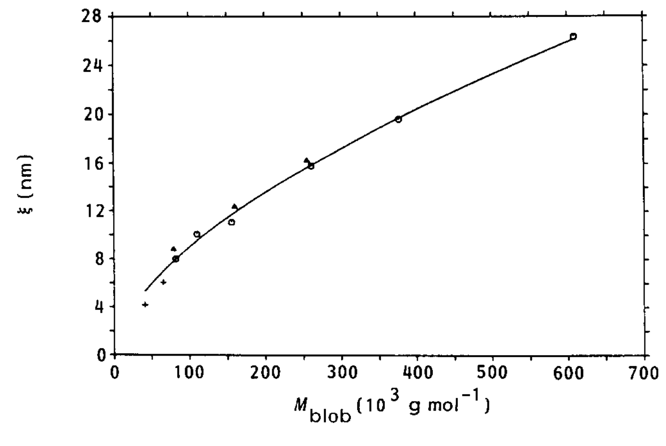

Figure 7 Screening length ξ *versus* molar mass of blobs M_{blob}: (○) $M_w = 8.45 \times 10^6$, (△) $M_w = 5.65 \times 10^6$ and (+) $M_w = 1.44 \times 10^6$ g mol^{-1} (see *Table 2*)

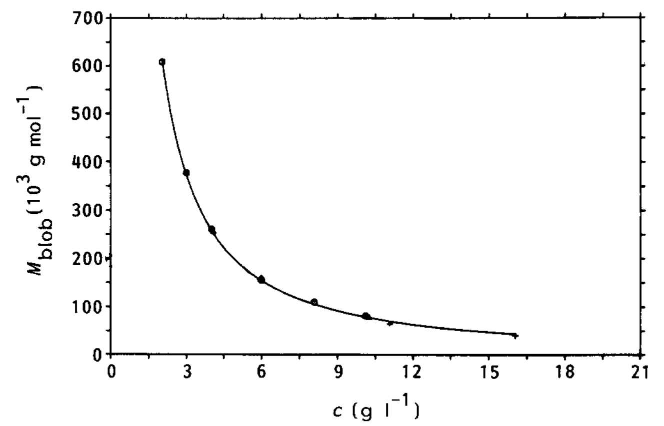

Figure 8 Molar mass of blobs M_{blob} *versus* concentration c: (○) $M_w = 8.45 \times 10^6$, (△) $M_w = 5.65 \times 10^6$ and (+) $M_w = 1.44 \times 10^6$ g mol^{-1} (see *Table 2*)

Table 3 Correlation length a and $\phi_2 M_{LRH}$ evaluated with program LOREQ1

M_w (g mol^{-1})	c (g l^{-1})	a (nm)	$\phi_2 M_{LRH}$ (g mol^{-1})
8.45×10^6	2.98	75.8 ± 56.4	49 200 ± 29 000
	4.00	92.4 ± 36.2	83 700 ± 45 000
	5.97	85.8 ± 14.7	105 000 ± 23 000
	8.07	111.2 ± 12.8	203 000 ± 45 000
	10.11	103.8 ± 8.4	196 000 ± 28 200
5.65×10^6	4.07	112.5 ± 16.4	374 000 ± 103 000
	5.97	105.8 ± 14.0	223 000 ± 52 000
	10.24	104.8 ± 8.6	191 000 ± 28 000
1.44×10^6	4.90[a]	92.5 ± 40.3	46 800 ± 29 000
	7.00[a]	92.6 ± 85.5	14 500 ± 19 100
	11.07	96.7 ± 17.4	51 400 ± 14 500
	16.04	98.1 ± 16.0	37 400 ± 10 000

[a] $c < c^*$

detectable according to the results of Gan *et al.*[11] for solutions of PS in dioxan. The fluctuation of $\phi_2 M_{LRH}$ is statistical and the values show no dependence on concentration. They are lower for solutions of the PS with the smallest molar mass than for solutions of the two higher-molar-mass samples. Because $\phi_2 M_{LRH}$ is a product, no conclusion can be made about the segment density of LRHs.

The Zimm plots in *Figure 3* show no linear range. Therefore, the evaluation receives an erroneous interpretation according to program LOREQ1 with the free selective quantities in equation (10). However, parameters ξ and M_{blob} in equation (10) can be calculated as a function of concentration by means of the scaling relationships (11a) and (11c). For the evaluation of these scattering curves, the program LOREQ1 was modified. Thus ξ as a nonlinear parameter was calculated according to equation (11a) and fixed. The other three quantities in equation (10) were determined by means of modified program LOREQ1. *Figure 9* shows one fit. The straight line above the measuring points shows the Ornstein–Zernicke scattering again (first term in equation (10)). In comparison with *Figure 5*, this straight line is far away from the measuring points. The agreement between the fitted and the measured curves is good. In *Table 4* the calculated values of the screening length and the molar mass of blobs are listed together with quantities obtained according to the modified program LOREQ1.

The results obtained for M_{blob} agree reasonably well by calculation and fitting, respectively. The mean correlation lengths a of LRHs also indicate no variation with concentration and their amounts correspond to values listed in *Table 3*.

CONCLUSIONS

Independent of the molar mass of three investigated PS samples, the onset concentration for excess scattering is located at concentration $c \sim 4$ g l^{-1}. The excess scattering increases with concentration and finally will be dominant. The excess scattering curves can be described very well by a four-parameter model. The parameters were determined by a least-squares method. Good agreement

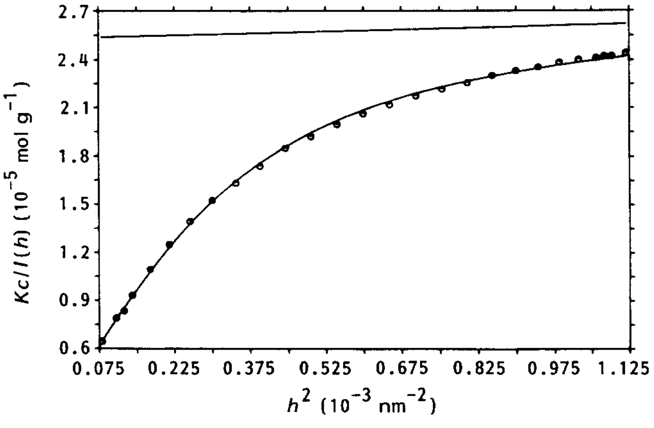

Figure 9 Fit with modified program LOREQ1 (ξ = constant = 5.4 nm) to a measured scattering curve (see text) for PS2/benzene: $M_w = 5.65 \times 10^6$ g mol^{-1}, $c = 17.96$ g l^{-1}

Table 4 List of parameters (see text) obtained from light scattering curves in *Figure 3*

c (g l^{-1})	ξ (nm) (eq. (11a))	M_{blob} (g mol^{-1}) (eq. (11c))	M_{blob} (g mol^{-1}) (LOREQ1)	a (nm) (LOREQ1)	$\phi_2 M_{LRH}$ (g mol^{-1}) (LOREQ1)
14.09	6.5	52 100	55 000	94.7	371 000
17.96	5.4	38 300	39 400	89.2	307 000
24.82	4.2	25 400	27 000	94.1	419 000

has been found between the evaluation of screening length ξ and molar mass M_{blob} according to the scaling relationships for semidilute solutions and theory. The mean correlation length of LRHs is independent of concentration and molar mass of polymers in solution within error limits of ~ 100 nm. The weight fraction of polymer segments of LRHs has to be very small, otherwise the model for evaluation must not be applied. Because $\phi_2 M_{\text{LRH}}$ is a product, no conclusion can be made about segment density of LRHs.

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