

Light and neutron scattering studies of excess low-angle scattering in moderately concentrated polystyrene solutions

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(Received 27 March 1984; revised 25 July 1984)

The light scattering (*LS*) and small-angle neutron scattering (*SANS*) behaviour of semi-dilute solutions of polystyrene has been determined in both 'good' and 'theta' solvents. Above a critical concentration related to chain overlap, an excess small-angle scattering component is in evidence for scattering vectors, q , such that $qR_g < 1$. Application of a number of recent solution scattering theories fails to account for the small-angle scattering observed. The inter- and intramolecular scattering functions are measured experimentally through characterization of the *SANS* behaviour of solutions containing mixtures of polystyrene and perdeuteropolystyrene. The resultant intermolecular scattering functions depend on the fraction of labelled chains, indicating clearly that the solutions contain large scale fluctuations. *LS* studies support this hypothesis and further show that the presence of these fluctuations is reproducible, yet dependent on the solution preparation procedure. Similar behaviour is observed in screening length measurements. The excess low-angle scattering is well characterized by the Debye-Bueche random two-phase model, which is subsequently used to estimate the characteristic dimensions of the long-range fluctuations.

(Keywords: semidilute; polymer; solutions; scaling; scattering; correlations)

INTRODUCTION

Recent advances in polymer solution theories¹⁻³ have generated considerable interest in the behaviour of semi-dilute and concentrated polymer solutions. One important prediction resulting from these theories pertains to the structure of such solutions. Above a chain overlap concentration, c^* , the solution is assumed to be uniform, with a structure specified by a single length scale, ξ , the screening length. Experimentally, the screening length is easily extractable from scattering experiments, wherein the structure factor is⁴:

$$S(q) = \frac{1}{q^2 + \xi^{-2}} \quad (1)$$

This scattering function applies for the range of scattering vector $R_g^{-1} < q < L^{-1}$, where R_g is the radius of gyration and L is the persistence length. The Lorentzian form has been verified by small angle neutron scattering⁵ (*SANS*), light scattering⁶ (*LS*), and X-ray scattering⁷ (*SAXS*) experiments.

A number of scattering studies, however, have presented intriguing results for the range of scattering vector $q < R_g^{-1}$. In this region, excess scattering has been observed leading to deviation from the Lorentzian form factor, and suggesting that a second correlation length is required to describe the solution structure. This 'anoma-

lous' scattering has been documented in *LS* investigations spanning the last two decades⁸⁻¹⁹ as well as in recent *SANS* experiments²⁰. There is a strong inclination to dismiss the findings of these investigations by attributing the excess scattering to the effects of dust or insoluble polymer. The results of the previous studies, however, suggest that this is not a spurious effect, in that the anomalous excess scattering is found to correlate with a number of experimental factors including molecular weight, solvent quality, and concentration, in addition to the procedures for solution preparation.

Specification of a structural origin for the anomalous scattering has proven to be a difficult task in previous studies for a number of reasons. First of all, an appropriate theory for the scattering from concentrated solutions in the range $q < R_g$ was lacking. In addition, the light scattering technique is limited to determination of the total structure factor, and cannot resolve the inter- and intramolecular scattering functions. Consequently, analysis of the light scattering behaviour required a number of assumptions regarding these scattering functions.

These specific difficulties have now been removed as a result of the advent of the small angle neutron scattering technique, and associated developments in scattering theories. A general scattering theory for concentrated polymer systems has recently been proposed by Benoit and Benmouna²¹, and there now exist a number of experimental *SANS* methods for the determination of the

intermolecular and intramolecular scattering functions²²⁻²⁵. The present paper makes use of these new developments in order to reexamine the origin of excess low angle scattering in concentrated polystyrene solutions in both good (benzene) and poor (cyclohexane) solvents.

EXPERIMENTAL

SANS measurements

Neutron scattering experiments were carried out on the D11 and D17 SANS facilities at the Institute Laue Langevin in Grenoble, France. Solutions were contained in 1.0–2.0 mm thick quartz cells of circular cross section. The cells were held in a metal block with provision for temperature control using a recirculating water bath. The incident beam was defined by a 1.0 cm diameter diaphragm placed in front of the sample cell. Untreated scattering profiles were corrected for detector sensitivity using water as a flat scatterer, and compensation was made for sample adsorption. The incoherent scattering background was subtracted by measuring the SANS of a solution in which the same amount of ethyl benzene had been substituted for polystyrene. Intensities were recorded with a 64 × 64 element two-dimensional position sensitive detector at sample to detector distances of 10.53 m (D11) and 2.82 m (D17). The nominal wavelengths were 9.97 Å (D11) and 11.4 Å (D17).

The solutions studied consisted of polystyrene, prepared by anionic synthesis, in solution with either benzene, a good solvent, or cyclohexane, a theta solvent at 34.6°C⁸. Solutions were prepared by direct dissolution of the polymer in the appropriate amount of solvent followed by equilibration for several days. The solutions were then transferred to the quartz scattering cells approximately one-half to one hour before the SANS measurements. Specific cleaning procedures were not applied to solutions for SANS experiments.

SANS measurements of polystyrene ($M_w = 59\,000$) in poor solvent (d_{12} -cyclohexane) were carried out at temperatures of 25°, 40° and 60°C. Solutions were equilibrated at the measurement temperature for approximately 30 min before the measurement. SANS measurements of polystyrene in good solvent (benzene) were carried out for molecular weights ranging from 5300 to 99 000. Both systems were studied for a variety of concentrations both

above and below the chain overlap concentration, c^* . Additional experiments to determine the intra- and intermolecular scattering functions were performed on solutions containing mixtures of unlabelled and perdeutero styrene dissolved in mixed benzene solvent. The solvent contrast was adjusted to match that of unlabelled polystyrene by mixing unlabelled and perdeutero benzene. Characteristics of the SANS solutions are detailed in Table 1. All polymer samples were synthesized in Dr Picot's laboratory in Strasbourg.

LS measurements

Measurements of LS intensity were recorded with a FICA 50 photogoniometer. Polymer solutions were held at a constant temperature of $25 \pm 1^\circ\text{C}$ in a refractive index bath containing xylene. The linearly polarized radiation had a wavelength of 546 nm as selected by a green filter placed in front of the mercury arc source. A benzene standard was used to calibrate the instrument. The sample studied was polystyrene ($M_w = 3 \times 10^6$) in benzene, as described in Table 1. Zimm analysis of dilute solutions of this polymer leads to values of $R_g = 1010 \text{ \AA}$, $A_2 = 2.65 \times 10^{-4} \text{ mol cm}^3 \text{ g}^{-2}$, and $M_w = 3 \times 10^6$, in excellent accord with the results of Decker²⁶.

Concentrated solutions were prepared from dilute stock solutions that had been carefully cleaned by centrifugation at 10 000 r.p.m. for 90 min. The decanted dilute solutions were placed into degreased and meticulously cleaned scattering cells fitted with sintered glass filters that prohibited the entry of dust particles, but allowed solvent to be withdrawn or added. The cells were connected to a vacuum rack by means of a ground glass joint at the top of the cell, whereupon concentration of the solutions was accomplished by either freeze drying, or constant temperature solvent evaporation. Concentration of the solutions was carried out slowly over a period of one to two days. Agitation was not applied either during or after the concentration step. There were no detectable differences in the scattering behaviour of solutions prepared by either evaporation or freeze drying.

RESULTS

The light scattering from concentrated polystyrene in benzene solutions (Figure 1) illustrates behaviour similar

Table 1 Solution characteristics

Polymer	Solvent	$M_w \times 10^{-4}$	R_g (Å)	C^* (g cm ⁻³)*	A_2 (mol cm ³ g ⁻²) × 10 ⁻⁴
Polystyrene (PSH)	Benzene (BzH)	300	1010	4.84×10^{-3}	2.65
PSH	d_{12} -cyclohexane (25° C, 40° C, 60° C)	5.9	69† (@ 34.6° C)	0.30 (@ 34.6° C)	0† (@ 34.6° C)
PSH	d_6 -benzene (BzD)	5.9	100††	0.098	* *
		2.3	57††	0.21	* *
		1.2	39††	0.34	* *
		0.53	24††	0.64	* *
Polystyrene (PSH) +	5.25% BzD +	5.9 (PSH); 6.0 (PSD)	100††	0.098	* *
Poly(d_8 -styrene) (PSD) (PSD)	94.75% BzH	9.8 (PSH); 9.9 (PSD)	136††	0.064	* *

* Calculated from $C^* = M_w/N_A R_g^3$

† Claude Picot, private communication

†† Estimated from $R_g = 0.145 M_w^{0.595}$ [26]

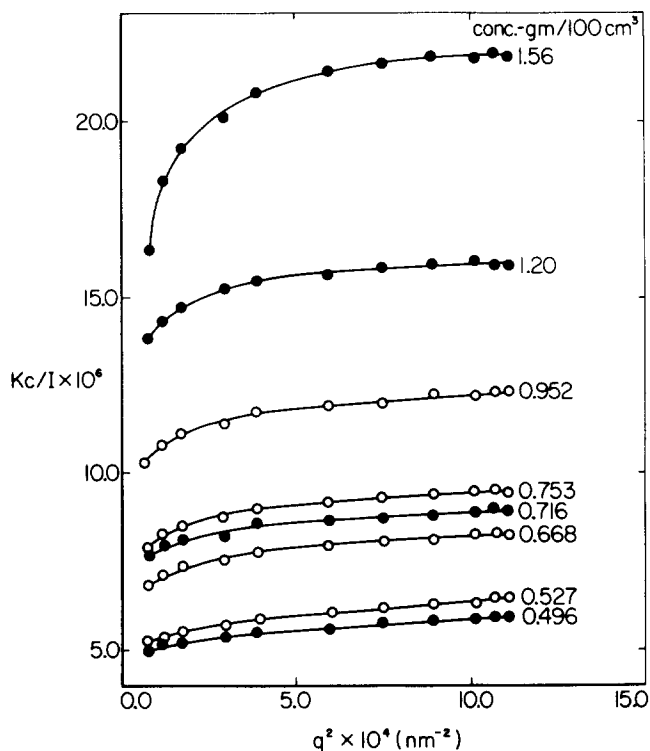


Figure 1 Modified Zimm plots of light scattering measurements of $M=3 \times 10^6$ polystyrene in benzene as a function of concentration. (●) solutions prepared by slow evaporation; (○) solutions prepared by subsequent redilution

to that observed in previous studies. An excess low angle component is in evidence for the scattering vector range approximated by $q < R_g^{-1}$. The abnormal behaviour becomes visible above a concentration of $\sim 5 \times 10^{-3} \text{ g cm}^{-3}$. This compares well to the estimated chain overlap concentration of $4.84 \times 10^{-3} \text{ g cm}^{-3}$ (Table 1). The definition of the overlap concentration as $c^* = M/N_A R_g^3$, where N_A is Avogadro's number, is rather arbitrary, and thus the apparent direct correspondence may be coincidental.

This LS abnormality is reproducible as evidenced in Figure 1. However, it is also strongly dependent on the particular sequencing of steps involved in the solution cleaning and preparation procedure. This dependence is clearly indicated in Figure 2. In this Figure, the open circles correspond to a solution prepared by centrifugation of a dilute solution, followed by slow solvent evaporation to attain the desired final concentration. The low-angle anomaly is clearly visible in this solution. Upon recentrifugation of this same concentrated solution, the curve denoted by crosses is obtained. In the recentrifugation process, the excess scattering apparently disappears. The scattering profile resulting from this process is nearly identical to that obtained from a solution of the same concentration which was prepared and centrifuged directly, as represented by the filled circles in Figure 3. This sensitivity to the centrifugation process was not observed in studies by Hager *et al.*¹⁶, but was documented in the work of Dautzenberg¹²⁻¹⁵.

SANS measurements produced results similar to those observed by light scattering. A representative plot is given in Figure 3. Again anomalous scattering appears above a critical concentration approximated by c^* , and below the q^{*2} value associated with R_g^{-2} . Essentially identical results are obtained for solutions containing polymer of

molecular weight 5300, 12 000, 23 000 and 59 000. Figure 3 also demonstrates the reproducibility of the SANS measurements.

With the SANS technique it is also possible to alter the solution contrast. In the case of unlabelled polystyrene (PSH) in benzene, this is accomplished using a mixed solvent of unlabelled benzene (BzH) and perdeutero benzene (BzD). Figure 4 shows the results of such studies for 0.3 g cm^{-3} solutions of $M_w=59000$ polystyrene in benzene. The scattering profiles are indistinguishable when normalized by their coherent scattering cross sections as described in Table 2, indicating that the

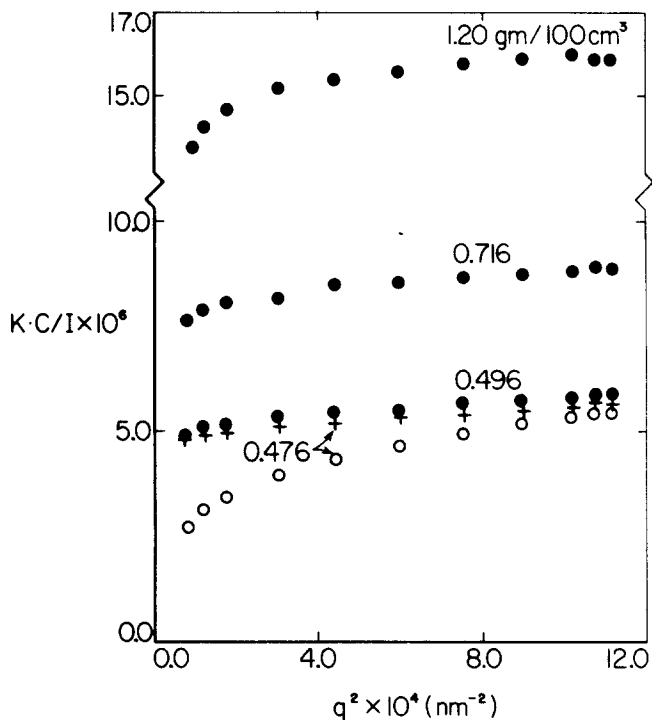


Figure 2 The effect of solution preparation method on light scattering profiles. (○) centrifuged dilute - concentrated by slow evaporation; (×) results upon recentrifugation of 0.476 g/100 cm^3 solution; (●) 0.496 g/100 cm^3 solution centrifuged directly followed by slow evaporation

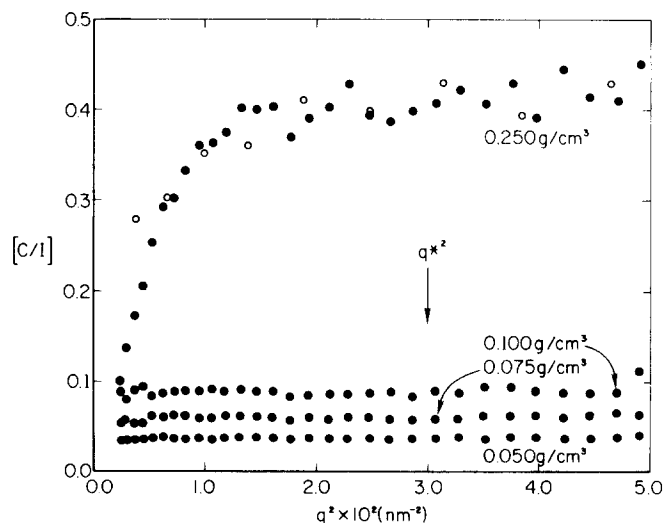


Figure 3 SANS profiles for PSH ($M_w=23\ 000$) in BzD. (●) data taken with the D11 instrument; (○) 0.3 g cm^{-3} solution measured on the D17 instrument

contrast for the excess scattering is of equivalent functional form to that of a homogeneous solution. A similar conclusion results from studies of 0.15 g cm^{-3} solutions.

These results indicate that the excess low-angle scattering is associated with the polymer molecules themselves, and is not the result of void formation, impurities, or multiple scattering.

The effect of solvent quality on the observed excess scattering was investigated by SANS measurements of PSH solutions in d_{12} -cyclohexane. Scattering intensities for PSH of $M_w = 59\,000$ were recorded in d_{12} -cyclohexane solutions at temperatures of 25° , 40° and 60°C , for polymer concentrations of 2%, 10%, 20%, 30% and 50%. These temperatures cover a range that spans both above and below the theta temperature (34.6°C), and the selected concentrations range both above and below the overlap concentration ($c^* \sim 0.3$ at 34.6°C).

The scattering behaviour of these solutions is essentially identical to that observed for PSH in benzene. Results for the 20% solution are representative of the general behaviour and are presented in Figure 5. Examination of the Figure reveals that at 25°C , the polymer solution is below the critical concentration but that at 40°C the solution is above the critical concentration. This is consistent with the interpretation that the overlap concentration is somehow related to the critical concentration for appearance of the scattering anomaly, since changing the temperature from 25° to 40°C would be accompanied by some chain expansion. The concentration dependence of scattering behaviour at fixed temperature is also consistent with this interpretation as the critical concentration for presence of the anomaly is found to decrease with increase in temperature.

The SANS technique also furnishes various means²²⁻²⁵ for determination of the intramolecular or

single chain scattering function, and intermolecular scattering function in concentrated polymer solutions. The simplest of these procedures, in terms of the final analysis, consists of preparing a solution of mixed PSH and PSD in a mixed solvent such as that listed in Table 1. The contrast of the PSH can be nulled by using a mixed solvent comprised of 5.25% BzD and 94.75% BzH. If the total amount of polystyrene present contains a fraction, x , of isotopically labelled polystyrene, and the PSH contrast matching with the solvent is realized, the scattering intensity may be written^{22,24,25}:

$$I(q,x) \sim xP(q) + x^2Q(q) \quad (2)$$

where $P(q)$ is the intramolecular scattering function and $Q(q)$ is an intermolecular scattering function. The two functions are obtained from measurements of solutions of equal concentration, c , containing different fractions, x , of isotopically labelled polymer. The functions $P(q)$ and $Q(q)$ are calculated from the intercept and slope of a plot of $I(q,x)/x$ as a function of x ^{22,27}.

An experiment of this type was carried out with $M_w = 59\,000$ polystyrene for the solutions described in Table 1. The results of measurements on these solutions are represented in Figure 6. The behaviour displayed in this Figure does not follow the prediction of equation (2), and plots of $I(q,x)/x$ versus x are not linear, making estimation of $P(q)$ and $Q(q)$ by this method impossible. This is clearly in evidence in Figure 6 as the anomaly

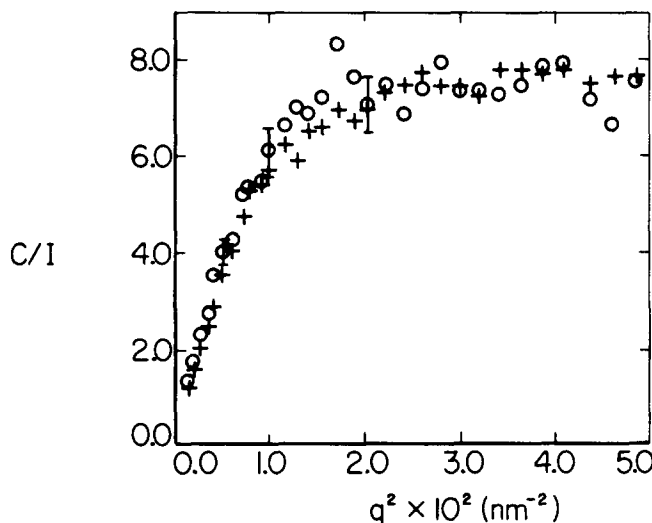


Figure 4 Contrast normalized SANS curves for PSH ($M_w = 59\,000$) in mixed benzene solvents. (x) S30K0; (o) S30K25

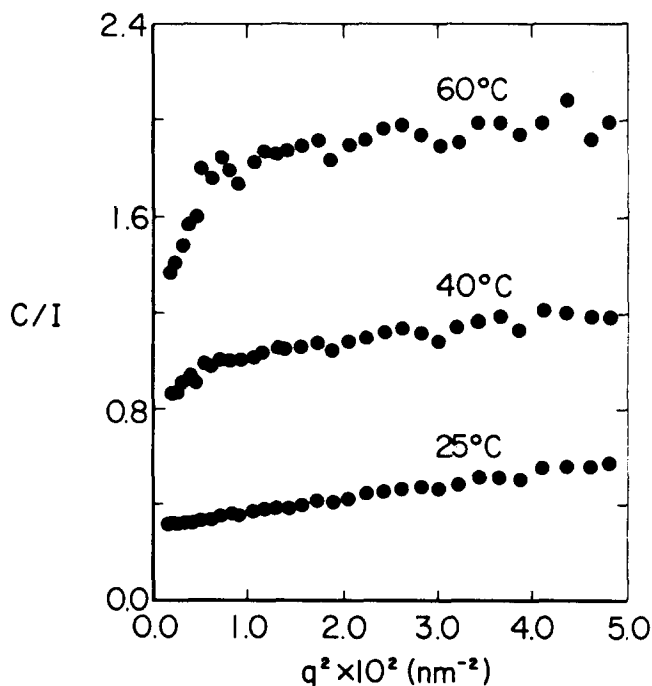


Figure 5 Temperature dependence of SANS for 20% solutions of PSH ($M_w = 59\,000$) in perdeutero cyclohexane

Table 2 Characteristics of polystyrene ($M_w = 59\,000$) solutions in mixed solvents

Solution	C_{PSH} (g cm^{-3})	Solvent	\bar{A}_{solvent} (10^{-12} cm)	σ_{coherent} (barn)
S30K0	0.30	BzD	7.99	552
S30K25	0.30	25% BzD + 75% BzH	6.43	299

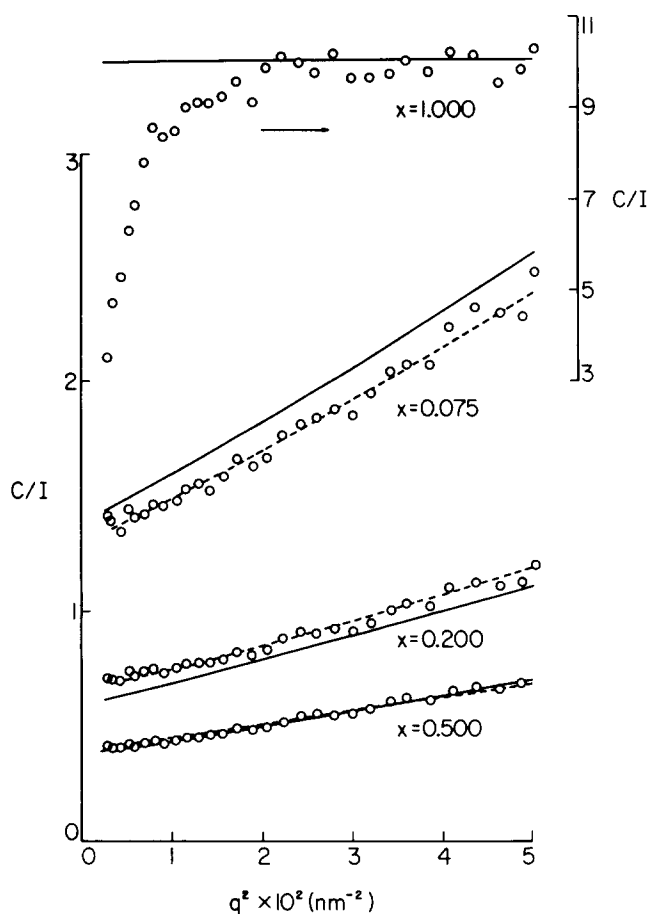


Figure 6 SANS profiles for 30% solutions of polystyrene ($M_w = 59\,000$) as a function of the fraction x , of deuterium labelled chains. (---) Fits of Benoit–Benmouna theory²¹ to individual curves; (—) result of the best universal fit

appears only in the solution with $x = 1.0$. Identical behaviour was observed for $M_w = 99\,000$ solutions in benzene.

The scattering intensities obtained from these contrast labelled solutions may also be compared to the scattering theory recently proposed by Benoit and Benmouna²¹. For a system of total concentration c , with a fraction, x , of labelled chains, the scattering intensity is predicted to be of the form:

$$\frac{MK_0xc}{I(q,x)} = \frac{1}{P(q)} + \frac{2A_2(c)Mxc}{1 + 2A_2(c)M(1-x)cP(q)} \quad (3)$$

where M is the molecular weight; $A_2(c)$ is the concentration dependent second virial coefficient; and K_0 is the contrast factor.

The fits of the Benoit–Benmouna theory are plotted with the experimental data in Figure 6. The dashed lines are the best fits to each individual scattering curve, obtained by adjusting the values assumed for the radius of gyration, the second virial coefficient, and a lumped constant to take into account the absolute intensity level. For this purpose, the single chain scattering function, $P(q)$, was assumed to be given by the Debye function^{28,29}:

$$P(q) = \frac{2}{u^2} [\exp(-u) - 1 + u] \quad (4)$$

where $u = q^2 R_g^2$. The solid lines in Figure 6 result from the

best fits using one set of universal parameters. In this calculation, the value of each parameter is extracted from the particular scattering curve which offers the greatest sensitivity to that parameter. The radius of gyration value is taken from the fit of the most dilute solution, $x = 0.075$; $A_2(c)$ is estimated from the most concentrated solution, $x = 1.00$; and the lumped constant is taken from the results on the solution with highest contrast factor and intensity, $x = 0.500$.

The resultant fits using both procedures are excellent excepting that of the $x = 1$ solution, for which the low angle anomaly appears. The best universal fit is observed for values of $R_g = 66.5 \text{ \AA}$ and $A_2(c) = 2.9 \times 10^{-3} \text{ mol cm}^3 \text{ g}^{-2}$. The radius of gyration obtained in this fit leads to a value of 0.056 for the quantity $R_g^2 c^{1/4} M^{-1}$. This compares to the universal value of 0.060 found previously for semi-dilute solutions of polystyrene in CS_2 ³⁰, which like benzene, is a good solvent for polystyrene.

Application of this theory to a 0.2 g cm^{-3} solution of $M_w = 99\,000$ polystyrene in benzene produced identical results. The Benoit–Benmouna fit described well the behaviour of solutions with x values of 0.1 and 0.6, but again failed to reproduce the scattering anomaly evident in the solution containing only labelled polystyrene. Parameters extracted from the best fit were $R_g = 110 \text{ \AA}$ and $A_2(c) = 2.4 \times 10^{-3} \text{ mol cm}^3 \text{ g}^{-2}$.

The inability of SANS theories to account for the excess low angle scattering coupled with the results of the centrifugation experiments indicate that the solutions are inhomogeneous in nature. Further characterization of these large scale fluctuations requires examination of some of the theoretical aspects of heterogeneous systems. Theoretical treatments of such systems^{31,32} have shown that the total intensity can be described in terms of contributions from density fluctuations [$I_\rho(q)$], as a result of molecular contrast, and contributions from the long-range inhomogeneities, [$I_c(q)$], as a result of phase structure or concentration fluctuations.

$$I(q) = I_\rho(q) + I_c(q) \quad (5)$$

This approach can be applied to the measurements on partially labelled solutions in order to provide insight into the observed anomalies in $I(q, x = 1)$. In this case the density fluctuation term may be approximated by (2) or (3). The long-range fluctuations may be described with the Debye–Bueche approach³³

$$I_c(q) \sim \bar{\eta}^2 \int_0^\infty \gamma(r) \frac{\sin qr}{qr} r^2 dr \equiv \gamma(q) \quad (6)$$

where $\bar{\eta}^2$ is the mean square fluctuation in concentration or contrast density, and $\gamma(r)$ is a correlation function describing the spatial distribution of these fluctuations. Incorporating (2) and (6) into relation (5) results in an approximate expression of the following form:

$$I(q,x) \sim xP(q) + x^2Q(q) + C'C(x)\gamma(q) \quad (7)$$

where C' is a constant and $C(x)$ is an unknown contrast function that depends on the fraction of labelled chains and describes the contrast of the inhomogeneities. If it is assumed that $P(q) = -Q(q)$, as is found in the bulk state²⁵

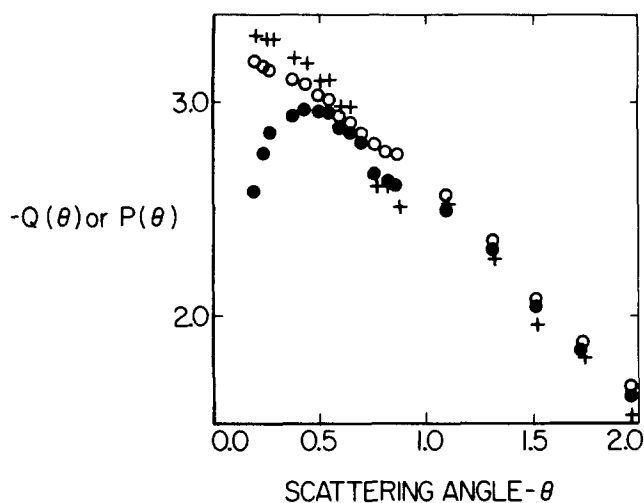


Figure 7 Inter- and intramolecular scattering functions for 0.3 g cm^{-3} polystyrene ($M_w = 59000$) in mixed benzene solvent. (\circ) $P(\theta)$; ($+$) $Q(\theta, x=0.5)$; (\bullet) $Q(\theta, x=1.0)$

an apparent intermolecular scattering function, in the presence of long range inhomogeneities, can be approximated as:

$$Q(q, x) \sim -P(q) + \frac{C'C(x)}{x^2} \gamma(q) \quad (8)$$

It is evident that the presence of long-range fluctuations provides a positive contribution to $Q(q, x)$ and causes a deviation from the equivalence of $Q(q, x)$ and $-P(q)$.

The apparent intermolecular scattering function can be calculated directly from the overall experimental scattering intensity by assuming that the single chain scattering function is approximated as $P(q) \sim I(q, x=0.075)/0.075$. The functions resulting from this procedure appear in Figure 7 as a function of the scattering angle, $\theta(q = 4\pi/\lambda \sin\theta/2)$. The $P(q)$ function obtained is fit well by the Debye function (4), using a value of $R_g = 72 \text{ \AA}$. The $Q(q, x=0.5)$ plots correspond well to $P(q)$ except for a slight negative deviation at small scattering angles, which arises from the radial distribution function. The finite distance of approach of the centres of gravity of polymer coils leads to a depletion of total scattering as has been modelled by Dautzenberg¹⁵. In this respect, the $Q(q, x=0.5)$ function does not display any significant abnormalities. In the case of $Q(q, x=1)$ the low-angle abnormality is clearly visible as a decrease in the negative magnitude of $Q(q, x=1)$ at small angles. This behaviour is qualitatively the same as that predicted by equation (8).

An approach similar to this may also be developed for the LS and SANS measurements of untagged polystyrene. The representation of scattering in terms of two individual correlation functions in this fashion has been used frequently for the description of inhomogeneous systems. Wu³⁴ has presented a theoretical treatment of the two correlation function approach, and similar approaches have appeared in studies of LS from inhomogeneous polymer blends^{35,36}, as well as aggregation in thermally reversible gels³⁷.

The historical approach relies on the assumption that the two correlation functions are of sufficiently different range, such that their contributions may be separated. For the semidilute solutions presenting the scattering anomaly, such a conditions is observed. The correlation length

of the solution is of the order of the screening length, ξ , while that of the inhomogeneity is much larger. The scattering expressions for the density fluctuations, equation (1), and concentration fluctuations, equation (6), lead to an expression for the scattering from such an inhomogeneous solution of the form:

$$I(q) \sim \frac{1}{q^2 + \xi^{-2}} + C'C(x)\gamma(q) \quad (9)$$

Separation of the two terms is accomplished graphically, in a manner described schematically in Figure 8. The Lorentzian contribution exhibits linearity in the Zimm representation, and is extrapolated to zero angle on this plot. The excess intensity arising from the homogeneities is defined as:

$$I_{\text{EX}}(q) \equiv c \left[\frac{1}{(c/I)} - \frac{1}{(c/I)_T} \right] = C''C(c)\gamma(q) \quad (10)$$

where (c/I) is the actual reduced intensity, $(c/I)_T$ is the extrapolated Lorentzian reduced intensity, and c is the concentration.

The excess intensity defined in this fashion is analysed within the framework of the Debye-Bueche theory (equation (6)). If the long-range fluctuations are random in nature, their spatial distribution is described by an exponential correlation function in distance, r :³⁸

$$\gamma(r) = e^{-r/a} \quad (11)$$

where a is an average correlation length. Incorporating this result into equation (6) leads to a scattering law of the form:

$$I_{\text{EX}}(q) = \frac{K\eta^2 a^3}{(1 + a^2 q^2)^2} \quad (12)$$

where K is a known optical constant. This scattering law may be fit to the excess scattering intensity by plotting $I_{\text{EX}}^{-1/2}$ versus q^2 . A typical plot of this type appears in

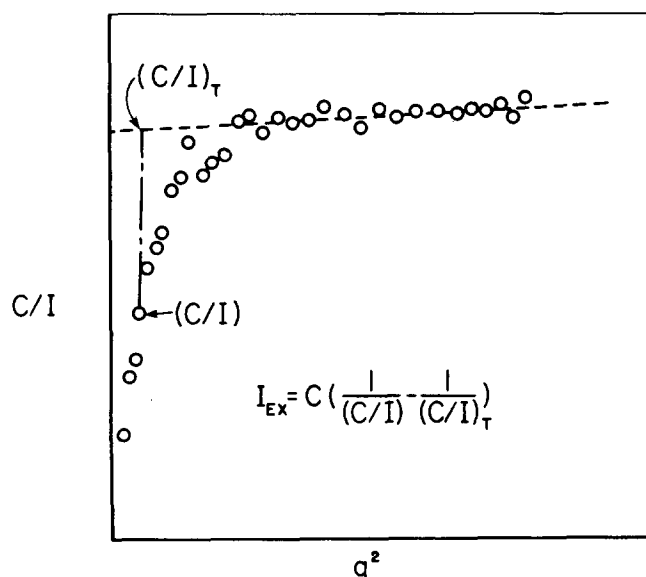


Figure 8 Graphical representation of the method used to calculate the excess low angle scattering intensity $I_{\text{EX}}(q)$

Figure 9. In this and all other plots investigated, linear relationships were obtained indicating excellent correspondence with the random correlation function. The original scattering curve can then be successfully reconstructed by summing the Lorentzian and Debye-Bueche contributions as shown in Figure 10. It should be noted that use of equation (1) was not successful in describing the excess scattering intensity.

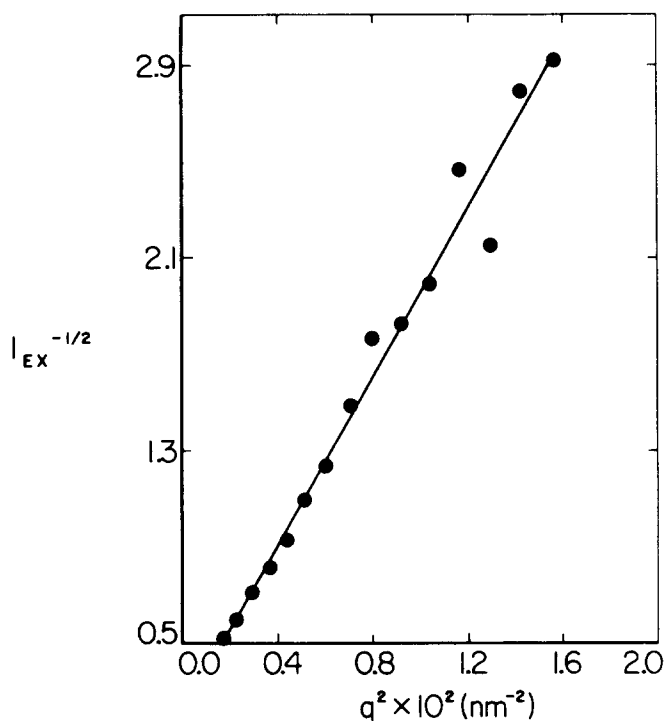


Figure 9 Debye-Bueche analysis of the excess scattering intensity for S30K0. (—) Best fit of Equation (12)

Table 3 Results of Debye-Bueche analysis for SANS of PSH ($M_w = 59\,000$) in BzD

Conc. (g cm ⁻³)	Temp. (°C)	R_g (Å)	a (Å)
0.30	25	~70	300
0.15	25	~75	250

Analysis of the SANS and LS data within this framework permits determination of the correlation length and mean square fluctuation in contrast density as described in Tables 3–5. The precision in absolute determination of the correlation length is low due to the complexity of the analysis, however it is seen that the correlation length is of the same order of magnitude as the estimated radius of gyration. Surprisingly, the mean square fluctuation is found to be essentially independent of either concentration or solvent quality.

Further interpretation of these values would require adoption of some structural model for the inhomogeneities³⁹. If the inhomogeneities are considered to be dilute for instance and formed of pure polystyrene (as would be consistent with the SANS contrast variation studies) the volume fraction of heterogeneities is found to be of the order of 10^{-9} . This value reflects only the minimum volume fraction, however, and one cannot uniquely specify a volume fraction unless the exact structure is known.

Separation of the two scattering contributions in equation (9) also provides an estimate of the screening length through analysis of the Lorentzian form factor given by equation (1). Application of this procedure to the LS data for 3×10^6 molecular weight polystyrene in benzene solutions leads to the screening lengths presented

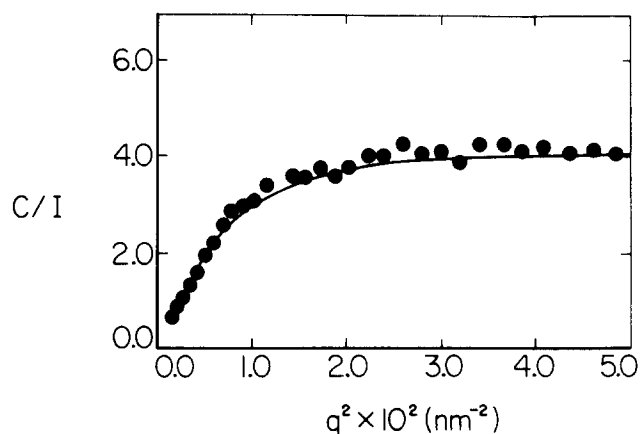


Figure 10 Reconstruction of SANS profile for S30K0 following Equation (9)

Table 4 Results of Debye-Bueche analysis for SANS of PSH ($M_w = 59\,000$) in d₁₂-cyclohexane

Conc. (g cm ⁻³)	Temp. (°C)	R_g (Å)	a (Å)	K_{η}^{-2} (relative)
0.30	25	~60	235	0.61
0.30	40	~60	220	0.56
0.30	60	~60	235	0.60

Table 5 Debye-Bueche analysis of LS for PSH ($M_w = 3 \times 10^6$) in BzH

Conc. (g cm ⁻³)	Temp. (°C)	R_g (c=0)	a (Å)	$\overline{\eta}^2$
7.16×10^{-3}	25	1010	1080	8.01×10^{-13}
7.56×10^{-3}	25	1010	1150	10.21×10^{-13}
9.52×10^{-3}	25	1010	1140	9.44×10^{-13}
1.20×10^{-2}	25	1010	1460	8.26×10^{-13}
1.56×10^{-2}	25	1010	1130	23.6×10^{-13}

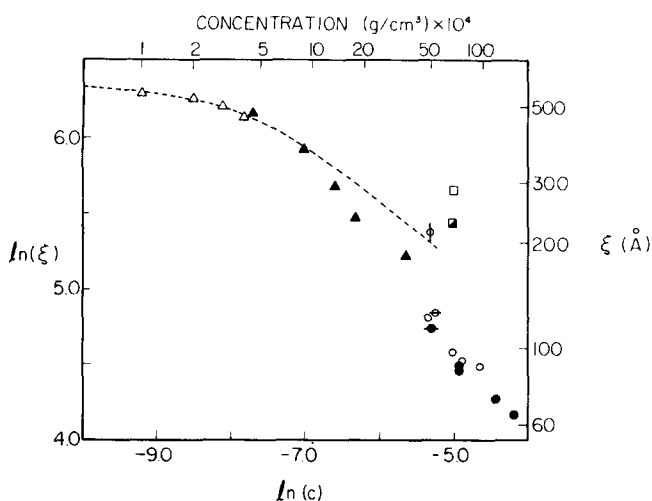


Figure 11 Screening lengths for polystyrene ($M=3 \times 10^6$ in benzene solutions. (□) 6.51 g cm^{-3} solution one day after preparation by evaporative concentration from a clean dilute stock solution; (■) the same solution after 16 days of equilibration. Other symbols explained in detail within text

in Figure 11. Some very interesting nonequilibrium behaviour is evidenced in this Figure. Up to a critical concentration of approximately $5 \times 10^{-4} \text{ g cm}^{-3}$, screening lengths are not a function of the procedure for solution preparation, and excess low-angle scattering is not observed. Above this concentration, the screening lengths depend upon the solution preparation procedure, and appear to depend upon presence of the low-angle anomaly. The open circle with vertical slash, for example, represents the solution of concentration $4.76 \times 10^{-3} \text{ g cm}^{-3}$, corresponding to the open circles in Figure 2. Upon recentrifugation, the excess scattering disappears as indicated by the crosses in Figure 2, and the screening length falls to that depicted by the circle with horizontal slash in Figure 11. This value compares well with that of the 0.496 g cm^{-3} solution in Figure 2 which was prepared by direct dissolution and centrifugation (filled circle with horizontal slash in Figure 11). It is not obvious however which solution preparation procedure represents equilibrium behaviour.

Ageing behaviour is also illustrated in Figure 11. Although the screening length of the 6.51 g cm^{-3} solution dropped considerably within 16 days, it still differs markedly from the solutions represented by the filled and unfilled circles in Figure 11. These latter solutions do not present appreciable excess low-angle scattering, and did not exhibit appreciable ageing behaviour. Further studies on the effect of ageing on the excess low-angle scattering (large scale fluctuations) are required in order to postulate any origin for these effects.

Careful examination of the screening length behaviour provides additional insight into the origin of excess low angle scattering. In the presence of the low-angle anomaly, the apparent screening length is much larger than that of solutions in which the anomaly has been minimized by recentrifugation. In fact, the values observed correspond fairly well to those predicted for non-penetrating polymer coils. In this case, an apparent screening length follows from the Zimm relation:

$$\xi_{\text{APP}} = R_g / (6cA_2M + 3)^{1/2} \quad (13)$$

This relation is indicated by the dashed line in Figure 11.

Agreement with this relation is observed for the dilute solutions (open triangles) as expected. As the concentration is increased, chain interpenetration is increased and the screening lengths deviate from this relation (filled triangles). Above the critical concentration ($\sim 5 \times 10^{-3} \text{ g cm}^{-3}$), the values for solutions exhibiting long-range fluctuations again correspond to those given by equation (13) suggesting that the polymer coils do not penetrate. As was mentioned earlier, this concentration coincides with our arbitrary definition of the overlap concentration c^* . This indeed seems coincidental, as the data for solid triangles suggest that overlap occurs significantly below this concentration.

The arbitrariness in definition of c^* is removed in a recent theory proposed by Schaefer⁴⁰. For 3×10^6 molecular weight polystyrene in benzene, an overlap concentration of $\sim 2 \times 10^{-4} \text{ g cm}^{-3}$ is predicted. This concentration is well below that for appearance of the non-equilibrium behaviour. It is interesting, however, that the critical concentration for anomalous behaviour, corresponds well to the crossover concentration from semi-dilute to marginal behaviour predicted to occur at $\sim 4 \times 10^{-3} \text{ g cm}^{-3}$. Analysis of screening length behaviour appears to confirm this value for the semi-dilute to marginal crossover⁴¹.

DISCUSSION

The results of light and neutron scattering experiments show clearly that excess small angle scattering in concentrated solutions is associated with the presence of large scale concentration fluctuations in solution. The observed excess scattering intensity is found to correspond well to the Debye-Bueche random two-phase model. Application of the model enables characterization of the mean square fluctuation in polarizability and the correlation length. Although the analysis does not lead to exact specification as to the structural nature of the long range fluctuations, the results of the present study can be used to examine previous explanations of the phenomenon.

Dautzenberg¹²⁻¹⁵ for example, attributed the anomalous scattering to the presence of preferential alignment of non-spherical polymer coils. The intermolecular scattering functions associated with Dautzenberg's model however do not correspond to those determined experimentally by the present SANS experiments.

Guenet, *et al.*¹⁹ suggested that anomalous scattering in atactic polystyrene solutions is found only for those solvents that promoted physical gelation as documented by Tan *et al.*⁴². In the present and previous studies however, anomalous scattering occurs for solutions in both cyclohexane and benzene, solvents which do not promote reversible gelation⁴². Guenet *et al.* did not examine these two particular solvents. There is a possibility that the polystyrenes studied herein may possess a higher syndiotactic content leading to gelation even in benzene and cyclohexane; however evidence for gel formation was not observed in any of the solutions tested. In addition, previous scattering studies of thermally reversible gels⁴³ led to correlation lengths of several thousand Angstroms, orders of magnitude larger than those determined presently. It appears then that the present phenomenon may be inherently different than that investigated by Guenet *et al.*

A number of previous models for excess low-angle

anomalous scattering have been based upon inhomogeneities in molecular interpenetration or network formation¹⁶⁻¹⁸. Although these models correctly account for the observed onset of excess scattering at concentrations corresponding to the chain overlap concentration, they are not consistent with many of the results of the present study. The dependence of excess low-angle scattering on solution preparation procedures, and the observed screening length behaviour, however, does support an interpretation involving chain interpenetration effects. This explanation is still very speculative, and does not provide a clear answer as to why the chains would not interpenetrate. A number of additional experiments are required to merit a more detailed discussion of this intriguing possibility.

The results of the present study do clearly show that a single length scale is inadequate in describing the scattering behaviour of concentrated polymer solutions. Although scaling theory implicitly assumes that these solutions are uniform, the possibility of large scale concentration fluctuations should not be excluded. The excluded volume blobs envisioned in scaling theory, for example, cannot be packed randomly in space as hard spheres due to connectivity constraints provided by individual chains. Large scale fluctuations may be correctly neglected when considering certain properties, however, their existence cannot be rejected on this basis alone since their presence may be related to some other observations.

CONCLUSION

The behaviour of solutions of polystyrene in both 'good' and 'theta' solvents has been studied by application of the light and neutron scattering techniques. Above a critical concentration, corresponding well to the overlap concentration c^* , an excess scattering component is observed for scattering vectors given by $qR_g < 1$. This behaviour is reproducible and is evidenced for a wide variety of molecular weights, in both cyclohexane and benzene solutions. Current scattering theories developed for homogeneous polymer solutions do not account for the anomalous small angle scattering component. These experiments confirm that anomalous scattering arises from the presence of long-range concentration fluctuations, with correlation lengths comparable to the radius of gyration of dissolved polymer.

ACKNOWLEDGEMENTS

This research was supported by a fellowship sponsored by the NSF-CNRS exchange of scientists programme and performed at the Centre de Recherches sur les Macromolécules in Strasbourg, France. The authors are grateful to

Dr J. M. Guenet for many helpful discussions, and to Dr C. Strazielle for assistance with the LS measurements.

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