Static screening length behaviour in polystyrene solutions

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The concentration dependence of screening lengths in polystyrene solutions is determined by light and neutron scattering measurements. The data support the existence of a marginal regime in the temperature–concentration diagram, inside which mean field behaviour is observed. In addition, it is found that polymer solutions conforming to either semidilute good or marginal behaviour can be described universally in terms of two common variables: a reduced correlation length, and a reduced concentration. Experimentally determined concentrations for crossovers between various regimes of solution behaviour are reported, and compared with quantitative predictions from a recent theory of Schaefer.

(Keywords: light scattering; neutron scattering; screening length; polystyrene solutions; benzene; cyclohexane)

INTRODUCTION

Theories of polymer solutions at finite concentration[1-5] describe the density–density correlation function in terms of a single parameter, ξ, referred to as the static screening length. In its original development[1], ξ describes the size of a region in the solution within which excluded volume interactions are 'screened'. Above a critical concentration for chain overlap, c^*, this screening length is predicted to follow various power laws in concentration, and become independent of molecular weight. Both mean field and scaling theories predict distinct power law exponents for various regions in concentration–temperature space. The exact values of the exponents predicted from these theories differ however.

The screening length may be determined experimentally by a scattering experiment, wherein the structure factor is[6]

$$S(q,c,\tau) \sim \frac{1}{q^2 + \xi^{-2}(c,\tau)} \qquad (1)$$

The reduced temperature τ is defined as $(T-\theta)/\theta$ where θ is the Flory temperature corresponding to ideal chain behaviour. This expression is valid for the range of scattering vector defined by $R_g^{-1} < q < L^{-1}$ where R_g is the radius of gyration and L is the statistical segment length. A number of experimental investigations of the static screening length behaviour of polymer solutions have been carried out using light (LS)[7,8], neutron (SANS)[6,9-11] and X-ray scattering[12,13] analyses.

These measurements have yielded data in support of both the mean field[1,4] (see e.g. refs. 7 and 12) and the scaling law[5] (see e.g. refs. 6 and 8) predictions.

These apparent discrepancies in solution behaviour led to the development of a modified temperature–concentration diagram that included the effects of chain stiffness[14]. The new temperature–concentration diagram, shown in *Figure 1*, contains an additional region referred to as the marginal regime. In terms of the blob concept, crossover to marginal behaviour occurs when the screening length becomes comparable to the size of a blob. Under these conditions, the polymer chain is nearly ideal since the excluded volume interactions are weak, and thus the associated perturbations are more appropriately described by mean field theory. Predictions of the screening length behaviour for various regions of the temperature–concentration diagram are listed in *Table 1*. For semi-flexible polymers, the temperature–concentration diagram is predicted quantitatively in terms of three parameters[15,16]: the polymer molecular weight; the characteristic ratio of chains in dilute solution; and the Flory interaction parameter, χ. The predicted crossover concentrations are listed in *Table 2*, where N is the degree of polymerization, and the stiffness parameter n is equal to one sixth of the characteristic ratio.

The predicted crossover behaviour is found to correspond favourably to the results of dynamic light scattering experiments with only a few exceptions[15]. A quantitative comparison of these predictions for static screening lengths has not yet been carried out, and it is only recently that direct crossover behaviour from the semidilute theta to the semidilute marginal regime has been observed[17] in static measurements. In light of the deficiency in experimental measurements of static screening lengths, the present paper examines the concentration dependence and crossover behaviour of static screening lengths for solutions of polystyrene in benzene and cyclohexane. A broad range of concentrations and molecular weights are examined by application of the LS and SANS techniques.

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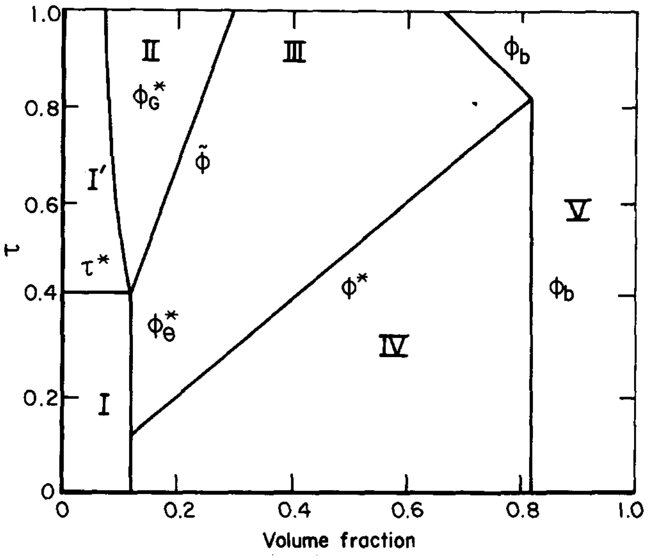

Figure 1 Temperature–concentration diagram for semi-flexible polymers in solution (after ref. 16)

Table 1 Predicted concentration dependence of the screening length

Regime	Flexible polymers[5]	Semi-flexible polymers[16]
I-Dilute θ	–	–
I′-Dilute good	–	–
II-Semidilute good	$c^{-0.75}$	$c^{-0.75}$
III-Semidilute marginal	–	$c^{-0.75}$
IV-Semidilute θ	c^{-1}	c^{-1}
V-Concentrated	c^0	c^0

EXPERIMENTAL

Light scattering measurements were recorded using a FICA 50 photogoniodiffusometer ($\lambda = 546$ nm). Polymer solutions were held at 25 ± 1°C in a xylene refractive index bath. Solutions were prepared by concentrating dilute stock solutions which had been cleaned by centrifugation. Small-angle neutron scattering experiments were carried out at the Institute Laué Langevin in Grenoble, France. SANS solutions were prepared by direct dissolution of the polymer in the appropriate amount of solvent. The signal-to-noise ratio for SANS was optimized by using perdeuterated benzene and cyclohexane as solvents.

LS studies were carried out for solutions of polystyrene in benzene incorporating polymer of molecular weights 1.6×10^6 (Polymer Laboratories), 3×10^6 or 9.1×10^6 (Polymer Laboratories). SANS measurements were performed on perdeuterated benzene and cyclohexane solutions containing polymer of molecular weight 5300, 12 000, 23 000 and 59 000. Unless otherwise indicated, the anionic polystyrenes were synthesized in Dr Picot's laboratory.

Experimental screeing lengths were determined by linear regression of the data plotted as $S^{-1}(q,c,\tau)$ against q^2. The extrapolated intercept $[S^{-1}(q,c,\tau) = 0]$ of such a plot is equal to $-\xi^{-2}$ as suggested by equation (1). This analysis was complicated however by the appearance of excess intensity in some solutions for $q < R_g^{-1}$ leading to strong deviations from linearity in these plots. This excess scattering contribution was the subject of intensive study in a previous report[18]. In the case of solutions for LS experiments, the excess scattering component could be minimized by recentrifugation of the solutions. This was not possible for SANS experiments due to the cell configuration. In this case, screening lengths were obtained by analysis of the linear portion of the $S^{-1}(q)$ *versus* q^2 plot (i.e. for $q > R_g^{-1}$). Further details pertaining to sample preparation, the experimental apparatus, and analysis of the excess small-angle scattering component are contained in the previous communication[18].

RESULTS AND DISCUSSION

The concentration dependence of the screening lengths of polystyrene solutions in benzene is presented in *Figure 2* for molecular weights ranging from 5300 to 9.1×10^6. The broken lines in this Figure are the apparent screening lengths in dilute solution that follow from rearrangement of the well-known Zimm relation

$$\xi_{\mathrm{app}}(c,M) = R_g(6cA_2M + 3)^{1/2} \qquad (2)$$

where M is the molecular weight and A_2 is the second virial coefficient. In applying the Zimm relation, dilute solution studies were carried out only on the $M = 3 \times 10^6$ polystyrene. The molecular weights of the other polymers were obtained from gel permeation chromatography experiments, and values of A_2 and R_g were estimated from the respective values for the 3×10^6 polystyrene. To accomplish these estimations the molecular weight dependence of the radius of gyration of polystyrene in benzene is taken as[19]

$$R_g(\text{Å}) = 0.145\,M^{0.595} \qquad (3)$$

The molecular weight dependence of the second virial coefficient is assumed to follow the scaling law prediction in the dilute limit[6] from which it follows that

$$A_2 = 0.00525\,M^{-1/5}\ \mathrm{mol\,cm^3\,g^{-2}} \qquad (4)$$

for polystyrene in benzene.

At high concentrations, the screening lengths of the low molecular weight solutions are seen to asymptote towards a c^{-1} dependence as predicted for the semidilute theta region. According to Schaefer[16], the volume fraction for

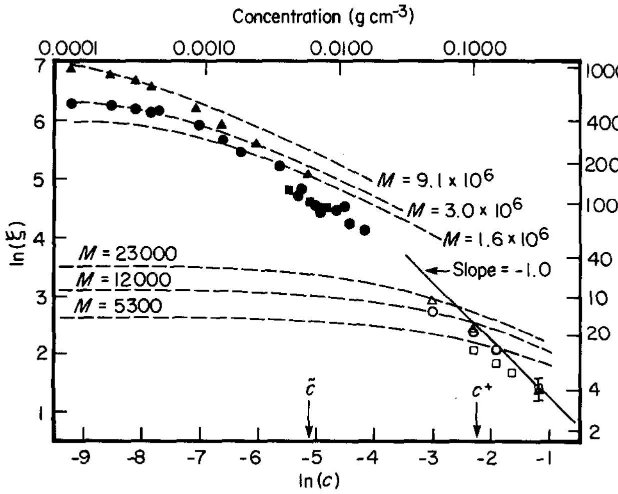

Figure 2 Concentration dependence of screening lengths for solutions of polystyrene in benzene. Open symbols are neutron scattering results (△, $M = 23\,000$; ○, $M = 12\,000$; □, $M = 5300$). Filled symbols are light scattering results (▲, $M = 9.1 \times 10^6$; ●, $M = 3.0 \times 10^6$; ■, $M = 1.6 \times 10^6$). Broken line corresponds to relation (2)

crossover to semidilute theta behaviour is given by $\phi^+ \simeq (1-2\chi)$ (ϕ^* in *Figure 1*) where χ is the Flory interaction parameter. Taking a value of $\chi = 0.451$,[16] and using a value of 0.95 for the specific volume of polystyrene, this gives a crossover concentration of $c^+ \simeq 0.1\ \mathrm{g\,cm^{-3}}$. This concentration corresponds well to the observed crossover as indicated in *Figure 2*. It is not clear from the data, however, whether the crossover concentration is independent of molecular weight, as predicted. In addition, the magnitudes of the screening lengths for the low molecular weights are smaller than the statistical segment length of polystyrene. It is generally predicted that the screening length remains constant once it attains a value equivalent to the statistical segment length[16].

The crossover from the semidilute theta regime to the concentrated regime is predicted to occur at $\phi_\theta \simeq n^{-1/2}$ (ϕ_b in *Figure 1*) or, in the case of polystyrene, a concentration of $c_\theta \simeq 0.81\ \mathrm{g\,cm^{-3}}$. Such behaviour is clearly not observed in *Figure 2*. The scattering technique however may be incapable of measuring the screening length at high concentrations. It is well known for example, that the scattering from a bulk homopolymer vanishes except for a term associated with thermal density fluctuations. Such behaviour has been confirmed experimentally[20], and suggests that the screening length goes to zero in the bulk state. This is contrary to the theoretical prediction but does correspond to the behaviour seen in *Figure 2*.

The predicted concentration for crossover from semidilute good to semidilute marginal behaviour is also denoted in this Figure, and corresponds to a value of (see *Table 2*) $\tilde{c} = 0.00615\ \mathrm{g\,cm^{-3}}$ for polystyrene in benzene. A crossover in behaviour is not obvious in *Figure 3* for the $M = 3\times10^6$ polystyrene. Marginal behaviour (i.e. $\xi \sim c^{-0.5}$) is clearly illustrated in *Figure 4*, however, which replots the data on a more expanded scale. The broken line has a slope of -0.75 according to the scaling law prediction, while the solid line is a best fit of the data given by

$$\xi_{\mathrm{exp}} = (7.4 \pm 1.1)\times10^{-8} c^{-(0.5\pm0.2)} \qquad (5)$$

This can be compared to the mean field prediction which, following a development similar to that of Cotton[7], may be expressed as

$$\xi_{\mathrm{th}} = \frac{f(\alpha)R_g}{2(A_2M)^{1/2}} c^{-1/2} \qquad (6)$$

Table 2 Predicted crossover behaviour of semi-flexible polymer solutions[16]

Crossover	Critical volume fraction
Dilute theta to semidilute theta	$\phi^*_\theta = \frac{3}{4\pi} N^{-1/2} n^{-3/2}$
Dilute good to semidilute good	$\phi^*_G = \frac{3}{4\pi} N^{-4/5} n^{-3/5} (1-2\chi)^{-3/5}$
Semidilute good to semidilute marginal	$\tilde{\phi} = \frac{3}{4\pi} \frac{(1-2\chi)}{n^3}$
Semidilute marginal to semidilute theta	$\phi^+ = (1-2\chi)$
Semidilute marginal to concentrated	$\phi_m = \frac{n}{(1-2\chi)}$
Semidilute theta to concentrated	$\phi_\theta = n^{-1/2}$

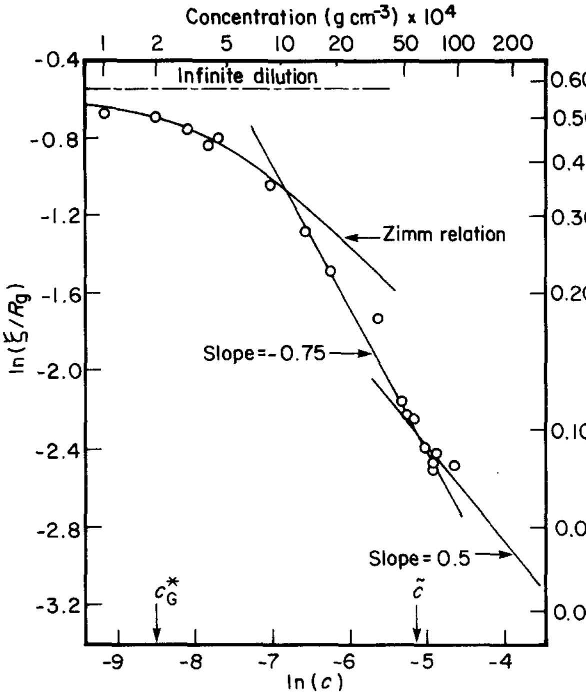

Figure 3 Concentration dependence of screening lengths for solutions of polystyrene ($M = 3\times10^6$) in benzene

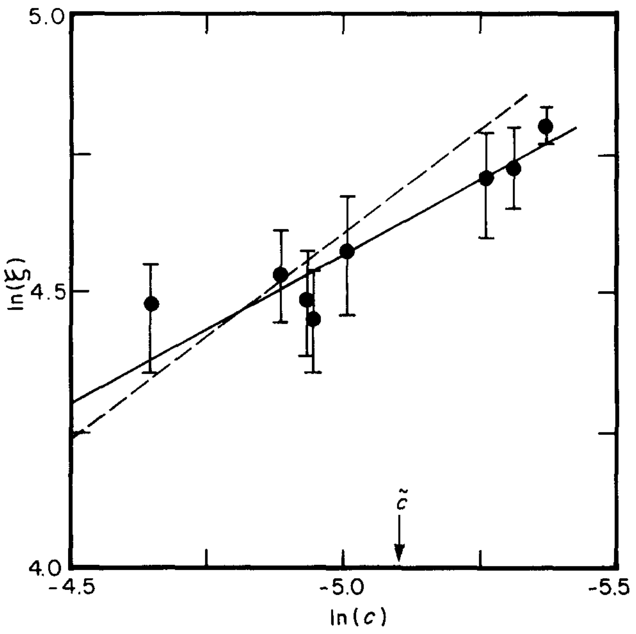

Figure 4 Concentration dependence of screening lengths for solutions of polystyrene ($M = 3\times10^6$) in benzene in the marginal semidilute regime. Solid line is mean field prediction (slope = −0.5) and broken line is scaling law prediction (slope = −0.75)

where $f(\alpha)$ is a function dependent on the chain expansion factor α. This function takes a value of unity for a theta solvent, and decreases monotonically with increase in solvent quality. For polystyrene in benzene the value of $f(\alpha)$ is approximately 0.66.[7] Substitution of the experimental values of $R_g = 1044$ Å and $A_2 = 2.65\times10^{-4}\ \mathrm{cm^3\,g^{-2}}$ for the $M = 3\times10^6$ polystyrene solutions into equation (6) leads to the following mean field prediction for the concentration dependence of the screening length:

$$\xi_{\mathrm{th}} = 12.2\times10^{-8} c^{-0.5} \qquad (7)$$

This expression agrees well with the experimental data represented by equation (5).

Referring again to *Figure 3*, the infinite dilution limit of the apparent screening length is seen to asymptote to a value of $R_g^{-1/2}$ as predicted by equation (2). As the concentration increases, the apparent screening length continues to follow the prediction of the Zimm relation until a concentration of *ca.* 1×10^{-3} g cm^{-3} is reached. At this point, a crossover to the scaling behaviour expected for the semidilute good regime (i.e. $\xi \sim c^{-0.75}$) is observed. Crossover from dilute good to semidilute good behaviour is predicted to occur for this polymer at $c_G^* = 1.96 \times 10^{-4}$ g cm^{-3} (see *Table 2*). The prediction clearly underestimates the concentration for the onset of scaling behaviour. This is a reasonable result considering that c_G^* refers only to the beginning of chain overlap, while observation of scaling behaviour requires substantial chain overlap (i.e. uniform segment density).

A similar interpretation provides an explanation for the screening length behaviour of $M = 59\,000$ polystyrene in cyclohexane solution at 40°C ($\theta = 40.2$°C[21]), as presented in *Figure 5*. A crossover from dilute theta to semidilute theta behaviour ($\xi \sim c^{-1}$) is apparent at a concentration of *ca.* 0.11 g cm^{-3}. The predicted concentration for this crossover is (see *Table 2*) $c_\theta^* \simeq 0.005$ g cm^{-3}. As in the case of benzene, the use of the overlap concentration severely underestimates the crossover to scaling behaviour.

Wiltzius *et al.*[8] have shown that the screening lengths of polymer solutions exhibit universality if properly normalized. The normalized parameters are a dimensionless correlation length ξ/R_g and a reduced concentration, X, where

$$X \sim A_2 M c \qquad (8)$$

For the purpose of the present work, the molecular weight dependence of the second virial coefficient is assumed to follow equation (4). The reduced concentration is then defined as

$$X = cM^{4/5} \qquad (9)$$

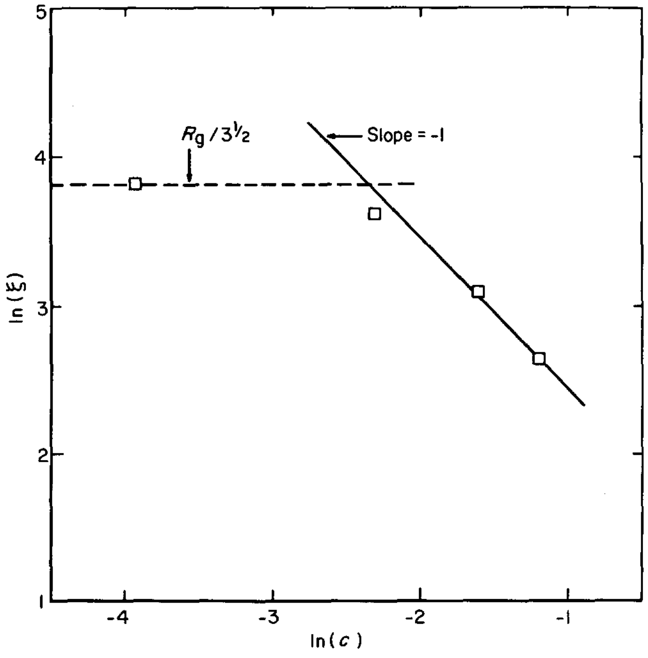

Figure 5 Screening length behaviour for solutions of polystyrene in perdeutero-cyclohexane at theta conditions ($T = 40$°C)

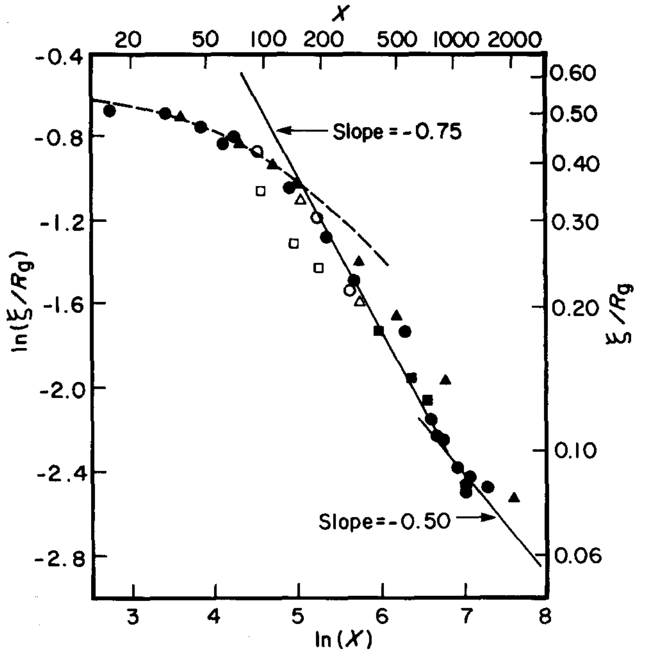

Figure 6 Reduced screening lengths as a function of the reduced concentration X, for solutions of polystyrene in benzene. Neutron scattering results (open symbols as for *Figure 2*); light scattering (filled symbols as for *Figure 2*)

A plot of reduced correlation length against reduced concentration appears in *Figure 6*, based on the data presented in *Figure 2*. In constructing the plot, the high concentration data that followed the c^{-1} dependence have been omitted. Although superposition of the data is less than satisfactory, this deficiency can be easily understood in terms of the Schaefer model. The correlation of Wiltzius *et al.* is based upon calculations of Ohta and Oono[22], valid only in the good solvent limit. A number of the experimental points in *Figure 6*, however, fall in the marginal regime as was shown earlier. In fact, all of the samples used in the SANS measurements have polymerization indices (i.e. molecular weights) that fall below the critical degree of polymerization (i.e. critical blob size) $N_\tau = 482$[16] for polystyrene in benzene. Under these conditions semidilute good behaviour is not realized, and marginal behaviour predominates.

The above arguments suggest that separate normalized plots should be constructed depending upon whether semidilute good or marginal behaviour is manifest. It is interesting to note, however, that the length and concentration scaling should be identical for the two regimes. This is evident from examination of the mean field expression given by equation (6), in which the ratio ξ/R_g is a function only of the reduced concentration $X \sim A_2 M c$.

Corresponding reduced plots for the two regimes of concentration dependence are shown in *Figures 7* and *8*. The selection of data points for the two correlations were made based upon consideration of the predicted crossover concentration $\tilde{c} = 0.00615$ g cm^{-3} and the critical polymerization index $N_\tau = 482$ (i.e. $M \sim 50\,000$). *Figure 7* shows the normalized data for the semi-dilute good regime. The result is similar to that of Wiltzius *et al.*[8] and shows universal asymptotic conformity to the $c^{-0.75}$ concentration dependence for semidilute solutions in good solvent. It should be emphasized that the range of

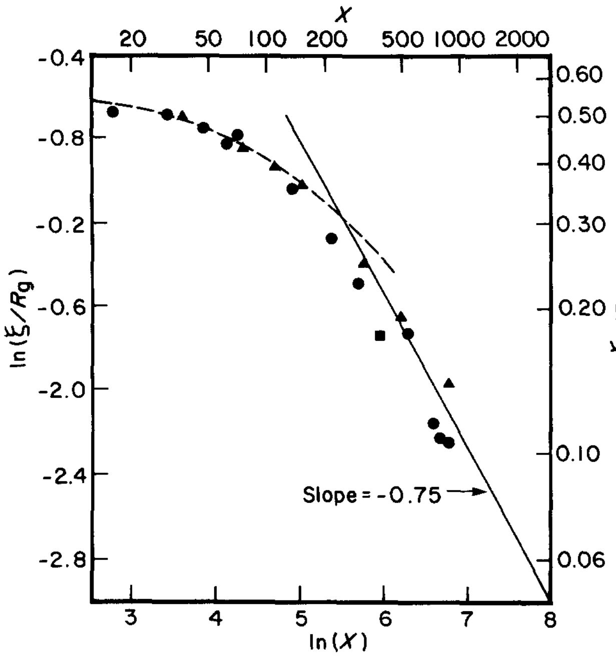

Figure 7 Reduced screening lengths as a function of the reduced concentration X, for solutions of polystyrene in benzene exhibiting semidilute-good regime behaviour (light scattering results symbols as for *Figure 2*, filled symbols)

concentration in which correspondence to semidilute scaling behaviour is found is relatively small, even for high molecular weight polystyrene.

A universal plot for marginal solutions appears in *Figure 8*. A best fit of the data leads to

$$(\xi/R_g)_{\mathrm{exp}} = (4.0 \pm 2.0)[X]^{-(0.52 \pm 0.07)} \qquad (10)$$

represented by the broken line in *Figure 8*. For comparison, the mean field prediction is given by the solid line. The theoretical prediction is obtained by inserting equations (4) and (9) into equation (6) and setting $f(\alpha) = 0.66$, from which it follows that

$$(\xi/R_g)_{\mathrm{th}} \simeq 4.55\, X^{-1/2} \qquad (11)$$

The agreement between the experimental and theoretical expressions is very good, especially considering that the virial coefficients were expressed by scaling relations rather than being measured directly. In fact, the theory and data become essentially superimposable if the value of $f(\alpha)$ is adjusted slightly.

The investigation of Wiltzius[8] *et al.* did not document any concentration dependence that could be associated with marginal behaviour, even though they did study solutions of polystyrene in methyl ethyl ketone (MEK), which is generally termed a 'marginal' solvent. This may be understood by considering the crossover concentration $\tilde{c}$. Assuming a value of $\chi = 0.458$[17] for polystyrene in MEK, the crossover is predicted to occur at $\tilde{c} = 0.0045\,\mathrm{g\,cm^{-3}}$. Examining the data contained in Figures 2 and 3 of ref. 8 reveals that only a few samples exceed this concentration. Unfortunately, the reduced concentration plot for these specific data points presents considerable scatter, making estimation of a reliable power law exponent impossible. Additional experiments to confirm the universality of solution behaviour in the marginal regime are clearly needed.

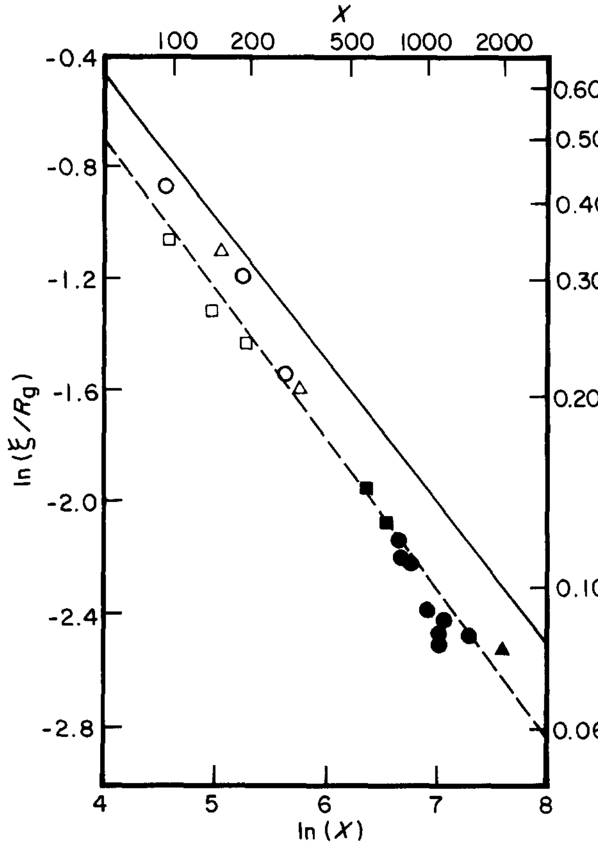

Figure 8 Reduced screening lengths as a function of the reduced concentration X, for solutions of polystyrene in benzene exhibiting semidilute-marginal regime behaviour. Neutron scattering results (open symbols as for *Figure 2*); light scattering results (filled symbols as for *Figure 2*). Broken line is best fit given by equation (10). Solid line is mean field prediction following equation (11)

The preceding discussion does emphasize the importance of adopting a set of consistent terminology of the description of polymer solution behaviour. One suggestion would be to employ the designations inherent to the temperature–concentration diagram of Schaefer[16]. In any case, it is evident that some degree of care should be exercised when referring to solvents as simply 'good' or 'marginal'. The actual behaviour of polymers' solutions is more complex.

CONCLUSIONS

The concentration dependences of screening lengths for solutions of polystyrene in benzene and cyclohexane support the general predictions of the temperature–concentration diagram proposed by Schaefer *et al.*[14]. Experimental values of concentrations for crossover between different regimes of solution behaviour correspond remarkably well to theoretical values calculated from the unified model for semiflexible polymers in solution developed by Schaefer[16]. In addition, universal behaviour is found for polymer solutions in both the semidilute marginal and semidilute good regimes when the screening length and concentration are properly scaled to yield reduced variables.

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