Screening Lengths in Concentrated Polystyrene Solutions in Toluene Determined Using Small Angle Neutron and Small Angle X-ray Scattering

Wyn Brown*

Department of Physical Chemistry, University of Uppsala, Box 532,
751 21 Uppsala, Sweden

Kell Mortensen

Risø National Laboratory, Physics Department, DK-4000 Roskilde, Denmark

George Floudas

Max-Planck Institut für Polymerforschung, Mainz, D-6500 Germany

Received June 22, 1992; Revised Manuscript Received September 9, 1992

ABSTRACT: Screening lengths have been measured for the polystyrene/toluene system using small angle neutron scattering and small angle X-ray scattering over the concentration interval 0.1–0.9 g/mL and in the temperature range from 5 to 70 °C. At the lower concentrations covering the semidilute regime ($c < 0.3$ g/mL) the concentration dependence agrees well with literature values: $\xi_s = (2.7 \pm 0.1)c^{-0.72\pm0.01}$/Å. At higher concentrations there is a stronger decrease in ξ_s to an approximately constant value: $\xi_s \approx 1.8$ Å. The observed intensities ($I(0)$) contain contributions from both density and concentration fluctuations and show a change in slope from a strong ($T > T_g$) to a weak ($T < T_g$) temperature dependence at the glass transition temperature.

Introduction

Different characteristic lengths have been introduced to describe the effects of chain overlap: ξ, ξ_s, and ξ_h. Here ξ is the correlation length for concentration fluctuations, ξ_s is the screening length of the excluded volume interactions, and ξ_h is the screening length for hydrodynamic interactions. The correlation length for concentration fluctuations (ξ) was first introduced by Edwards[1] and a discussion is given in ref 2. In very dilute solutions, intramolecular interactions are present and these manifest themselves as an excluded volume effect. If the polymer concentration is increased well above the critical overlap concentration (c^*) where the chains begin to mutually interpenetrate, the concentration fluctuations are significantly correlated and intermolecular interactions will progressively screen distant segments of the same chain from each other and diminish the range of the excluded volume interaction. The screening length describes the distance beyond which excluded volume interactions between any two segments on the same chain are not felt; the conformation is then that for a random walk process. We note that Fujita[3] distinguishes between ξ and the static screening length for excluded volume interactions (ξ_s) and states that the relationship between these quantities is unclear. Other authors (e.g., refs 4 and 5) imply that these lengths are identical.

Although in dilute solutions the correlation length for concentration fluctuations is of the order of the radius of gyration of the coil R_g ($\approx R_g/3^{1/2}$) and increases with molecular weight, the situation is entirely different in semidilute and concentrated solutions. In this case the characteristic length—which is usually called the screening length—is independent of molecular weight and decreases with polymer concentration; in the limit of high concentration it is anticipated to become the order of a bond length in the polymer chain. It was shown by Edwards that in the semidilute regime in good solvents, ξ_s, depends on polymer concentration as: $\xi_s \sim c^{-0.75}$, whereas at high concentrations as $c \rightarrow \infty$, $\xi_s \sim c^{-0.5}$. Subsequently, however, Daoud et al.[4] found experimentally a dependence of $c^{-0.72}$ in the semidilute range and they showed that the latter exponent results if correct renormalization is used. Application of mean field theory for a polymer in a good solvent correctly predicts the decrease in ξ_s as the concentration increases.[4,6,7] However, mean field theory predicts that ξ_s is concentration independent in a Θ system, a conclusion which is contradicted by experiment. Thus Kinugasa et al.[8] show a strong decrease in ξ_s for polystyrene in cyclohexane at 34.8 °C with an exponent of −1. Geissler et al.[9] have recently extended the concentration range up to a concentration of 0.71 g/mL at and below the Θ temperature. The power law exponent of −1 was confirmed.

The polymer solution was viewed by de Gennes[10] as made up of domains ("blobs") of dimension ξ_s which, as regards thermodynamic interaction, are independent of each other. Scaling theory predicts $\xi_s \sim c^{-\nu/(3\nu-1)}$ where the proportionality factor is independent of the molecular weight; ν is the excluded volume exponent defining the molecular weight dependence of the radius of gyration: $R_g \sim M^\nu$. Thus, in good solvents $\nu = 0.6$ and $\xi_s \sim c^{0.75}$. This relationship is strictly applicable only for strong excluded volume conditions and at infinite molecular weight. Nevertheless, strong experimental support has been forthcoming. An exponent of −0.72 was thus found for polystyrene in CS_2 using small angle neutron scattering (SANS) by Daoud et al.[4] The SANS measurements for polystyrene in toluene by King et al.[11] gave an exponent of −0.70 and the small angle X-ray scattering (SAXS) measurements of Hamada et al.[5] on the same system −0.77. An overview of the data collected for semidilute solutions in different good solvents using various techniques[12] (SANS, SAXS, and intensity light scattering) which encompass the concentration range up to about 0.3 g/mL led to the equation

$$\xi_s = (2.7 \pm 0.1)c^{-0.72\pm0.01}/\text{Å} \qquad (1)$$

We emphasize here the distinction between the static property (ξ_s) and that due to hydrodynamic screening ξ_h. The latter arises since chain overlap reduces the intrachain

0024-9297/92/2225-6904$03.00/0

hydrodynamic interaction and it has an analogous implication; i.e. pairs of segments of a given chain separated by more than ξ_h do not interact hydrodynamically. Muthukumar and Edwards[13] discuss these quantitites and suggest a numerical relationship between them. Experimentally, it is found[14] that $\xi_h/\xi_s \approx 2$. The screening length may be determined by neutron or X-ray scattering measurements and the structure factor is described by a Lorentzian scattering law

$$I(q) \sim I(0)/(1 + \xi_s^2 q^2) \qquad (2)$$

This expression is valid for a q-range extending between $R_g^{-1} < q < l^{-1}$, where l is the persistence length. The literature concerning the determination of static screening lengths is extensive (e.g., refs 4, 8, 9, 11, 14–16).

While our understanding of semidilute solutions is rather satisfactory, the same cannot be said for concentrated solutions. Investigations on more concentrated systems include the SANS experiments of Koberstein and Picot[15] which dealt in part with polystyrene in benzene up to a concentration $c \sim 0.3$ g/mL.

The variation of ξ_s with concentration in the very high concentration range in a good solvent which is the subject of this communication has not yet been explored. Neither do theoretical predictions exist for the concentration dependence of ξ_s as the bulk limit is approached. It is noted, however, that when the screening length becomes comparable to the persistence length (of the magnitude 8 Å for the PS chain), no further concentration dependence is anticipated.[17] However, it is known that scattering from a bulk homopolymer vanishes except for a term associated with thermal density fluctuations. This has apparently been confirmed experimentally,[18] and these data would suggest that the screening length approaches zero in the bulk state.

In conjunction with a dynamic light scattering and polarized Brillouin scattering study[19] on polystyrene in toluene encompassing the concentration range from 0.1 g/mL up to the melt, SANS and SAXS measurements were made on the same system, except that the solvent toluene was replaced by deuteriotoluene.

Experimental Section

Samples. Polymer/deuteriotoluene mixtures were prepared as described in ref 19 using carefully dried and vacuum distilled styrene. The mixtures were dosed into the stock ampule of a dust-free polymerization apparatus and degassed by several freeze–thaw cycles. The apparatus was then sealed. Dust was removed from the mixtures by repeated slow freezing in the ampule, followed by decantation. Finally, the cell containing the pure monomer mixture was sealed and placed in an oil bath. The thermal polymerization was carried out at 120 °C for 36 h. The conversion of the polymerization was about 96% at monomer fraction 0.1 and this increased with increasing monomer fraction to approaching 99% at the bulk end. The weight average molecular mass was 275 000 at $c = 0.9$ g/mL. The polymer volume fraction (Φ_p) was calculated from the starting monomer volume fraction (Φ) accounting for the density changes during polymerization. The radius of gyration corresponding to this MW is 210 Å, and the overlap concentration $c^* = 3M/4\pi R_g^3 N_A \approx 1.2\%$.

For SANS the polymer mixtures were transferred, using a thin-walled 5-mm glass tube, to 1-mm quartz cells from Hellma, Germany. The latter consisted of two circular plane windows and an annular spacer. The tube was allowed to sink under gravity (some hours for the highest concentrations) into the polymer mixture, thereafter slowly withdrawn and the polymer thread cut off. The mixture was then extruded under pressure into the quartz cells. The cell windows were sealed in place.

SANS experiments were performed using the Risø facility, which is a flexible instrument covering scattering vectors (q) in the range from 0.002 to 0.5 Å^{-1}. The scattering vector is given by $q = (4\pi/\lambda) \sin \theta/2$, where θ is the scattering angle and λ is the neutron wavelength. In the present study, two experimental settings were used, both with a neutron wavelength of 4 Å and with sample-to-detector settings of 1 and 5 m, respectively, exploring a q range of 0.01–0.4 Å^{-1}. Diameters of the source and sample apertures were 16 and 8 mm, respectively. A 40 mm diameter beamstop was used to mask the direct beam at the detector. The sample thickness of 1 mm results in transmission factors for the neutron beam of 0.895 and 0.635 for pure toluene and pure deuteriotoluene, respectively, and with the transmission of the polystyrene solutions varying linearly between these two values according to the polymer concentration. A small temperature dependence of the transmission factor was taken into account. Typical counting times were 0.5 and 2 h for the 1-m and the 5-m settings.

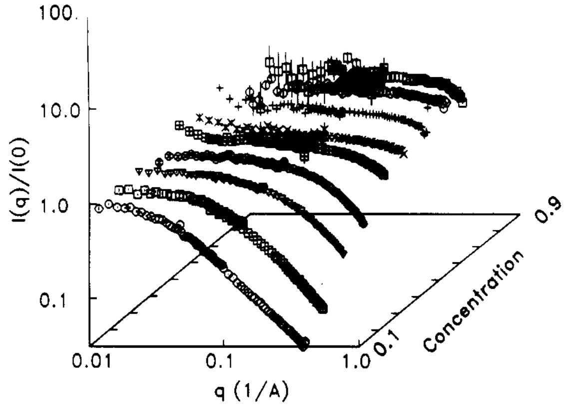

Figure 1. SANS experiments: log scattering intensity versus log q for the following concentrations in deuteriated toluene at 25 °C. Bottom to top in g/mL: 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9.

The two-dimensional scattering data were azimuthally averaged and corrected for background and detector response. The sample–background spectra were calculated from measurements of toluene and deuteriotoluene in quartz containers, taking the transmission factors into account. Correction for possible nonuniform detector response was made using the incoherent scattering of water. Using the toluene as a substitute for styrene in the background correction may give rise to small systematic errors. This is particularly the case for the solutions of high concentration in which the background data and the sample data differ by only small numbers.

SAXS measurements were performed using a Kratky camera equipped with a Braun one-dimensional position-sensitive detector. Cu Kα radiation ($\lambda = 1.542$ Å) was selected with a Ni filter from a Siemens generator operating at 35 kV and 30 mA. After subtraction of the background intensity and correction for absorption, the data were desmeared for slit length. The intensity of the primary beam (absolute units) was determined with a moving slit geometry, thereby avoiding scaling to a previously calibrated sample. The excess scattered intensity of the polymer was calculated by subtracting the intensity of toluene—scaled with concentration—at different temperatures. The fitting interval was from 0.028 to 0.1 Å^{-1} for $C_{PS} < 0.4$ and from 0.1 to 0.2 Å^{-1} for the $C = 0.8$ and 0.9 g/mL samples. The lower q limit for the concentrated solutions was chosen to avoid low-q "anomalies" in the data.

Results and Discussion

Figure 1 shows the SANS data at 25 °C for the samples covering the concentration range 0.10–0.90 g/mL. The curves are displaced for clarity. The scattered intensity, $I(q)$, is well approximated by the Lorentzian form (eq 2) as originally suggested by Zimm.[20]

Figure 2 shows the same set of data presented in the Zimm form with reciprocal intensity plotted against the square of the scattering vector ($1/(I(q)$ versus q^2), where $I(0)$ in eq 2 is obtained as the asymptotic scattering intensity at zero angle ($q = 0$). Such a relationship gives

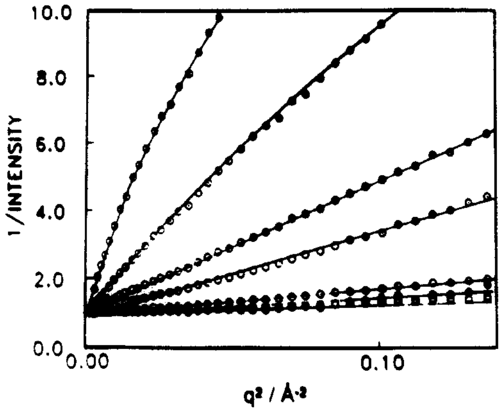

Figure 2. Inverse scattered intensity ($1/I(q)$) versus q^2 for polystyrene/toluene at 25 °C; SANS data corresponding to Figure 1 with the concentrations increasing from top to bottom in the diagram.

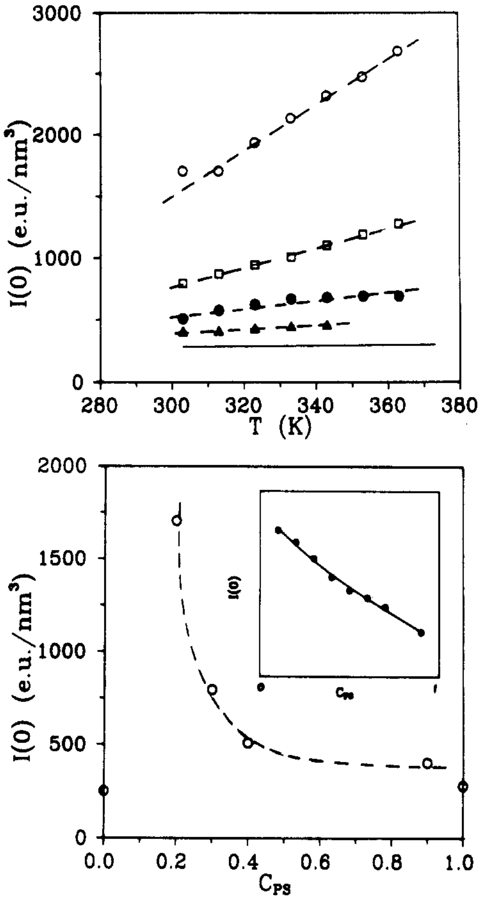

Figure 3. (a) Desmeared intensities $I(0)$ obtained from SAXS, plotted versus temperature for polystyrene concentrations: 0.2 g/mL (○); 0.3 g/mL (□); 0.4 g/mL (●); 0.9 g/mL (▲). The solid line is $I(0)$ for bulk polystyrene (ref 22). (b) Absolute intensities $I(0)$ from SAXS as a function of polystyrene concentration (30 °C). Insert: Data from SANS measurements at 25 °C covering the same concentration range as the SAXS measurements.

a straight line in the Zimm regime ($q\xi_s < 1$) according to eq 2. The curvature perceived at the two lowest concentrations in the higher q range thus represents data beyond the regime where Zimm behavior is found. The slope of the lines decreases systematically with increasing concentration and ξ_s^2 is obtained from the ratio of the initial linear slope to intercept. The narrow q range was chosen so that eq 2 would be strictly valid.

The intercept, $1/I(0)$, changes in a systematic way in both SANS and SAXS measurements. This is shown in Figure 3a where the absolute intensity $I(0)$ from SAXS measurements is plotted as a function of temperature for different PS concentrations.

In a one-component system in thermal equilibrium ($T > T_g$), $I(0)$ is given by

$$I(0) \sim \rho^2 k_B T K_T \qquad (3)$$

where K_T is the isothermal compressibility for the liquid and ρ is the average electron density. It has been discussed extensively before[21] that the observed intensities—contrary to the isothermal compressibility—show no discontinuity at T_g but only a change in slope from a strong ($T > T_g$) to a weak ($T < T_g$) temperature dependence.

In a two-component system, both concentration and density fluctuations can contribute to $I(0)$. Unless the system is free of scattering contrast—in which case only density fluctuations are important—separation of the two contributions to $I(0)$ without making assumptions about the length scales of the fluctuations involved[15b] is, at present, not possible. Thus, Koberstein et al. have assumed that the correlations lengths for density and concentrations fluctuations are very different and on this basis separate (graphically) in their SANS data the excess intensity due to concentration fluctuations. However, concentration fluctuations also contribute at higher q since density and concentration fluctuations are mixed. It is expected, nonetheless, that density fluctuations make the greatest contribution at high polymer concentrations whereas concentration fluctuations are dominant in the dilute/semidilute regimes. In accord with this expectation, we observe in Figure 3b higher $I(0)$ values for the 0.2 g/mL sample than for the more concentrated solutions. The steep temperature dependence for the lower concentrations (0.2 and 0.3 g/mL) is due mainly to the lower glass transition temperatures for these samples. It is noteworthy that the $I(0)$ value for the 0.9 g/mL sample is higher than for bulk polystyrene[22] due to the contribution of concentration fluctuations. Inset are the corresponding intensities (arbitrary scale) for the SANS data, which display the same trend but with a significantly weaker dependence on concentration.

The observation about sizable and—at present—nonseparable contributions from density and concentration fluctuations leads to another problem; eq 2 was obtained for concentration fluctuations alone. However, as demonstrated above with respect to Figure 3, in passing from the semidilute to the concentrated regime, density fluctuations become increasingly important. Therefore one can and should question the applicability of eq 2 in concentrated systems. On the other hand, lacking any theoretical predictions for this regime, we continue to employ this relationship at high concentrations.

Figure 4 shows a log–log plot of ξ_s versus concentration from SANS and SAXS data and values of ξ_s are listed in Tables I and II. The data for the two lowest concentrations (0.1 and 0.2 g/mL) are consistent with the slope of about −0.7 found for semidilute solutions as indicated by the linear portion of the curve given by the data of King et al.[11] The X-ray scattering data of Hamada et al.[5] for polystyrene in toluene are included and fall on the same line.

At higher concentrations, ξ_s decreases more strongly with increasing concentration and approaches an approximately constant value (~1.8 Å) above a concentration of 0.6 g/mL. As discussed above, this finding is dependent on correct background substraction and one should be aware of a possible systematic error when using toluene as a substitute for styrene in the background correction. However, the independent SAXS results adequately

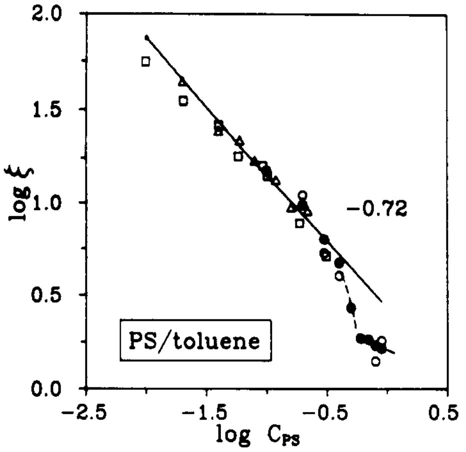

Figure 4. Double-logarithmic plot of screening length (ξ_s) versus polystyrene concentration (C_{PS}) in semidilute and concentrated solutions for $M_w = 2.75 \times 10^5$: (●) SANS, (○) SAXS; (△) SANS measurements of King et al.,[11] (□) SAXS measurements by Hamada et al.[5] for similar molecular weight polystyrenes. A continuous line of slope −0.72 is included.

Table I
Static Screening Lengths (ξ_s) (SANS) as a Function of Polystyrene Concentration in Toluene and Dynamic Screening Length ξ_h (from Dynamic Light Scattering[19])

	ξ_s/Å			
concentration/(g/mL)	7 °C	25 °C	70 °C	ξ_h/Å, 25 °C
0.1	15.1	15.1	17.3	30.4
0.2	9.6	9.7	10.6	17.4
0.3	6.2	6.3	6.6	11.5
0.4	4.6	4.7	4.9	7.7
0.5	2.7	2.7	2.8	6.3
0.6	1.8	1.9	1.8	4.9
0.7	2.0	1.8	2.0	
0.8	1.7	1.7	1.5	
0.9	1.7	1.6	0.9	

Static (SANS) Screening Length as a Function of Temperature

temperature/°C	ξ_s/Å, c = 0.9 g/mL	temperature/°C	ξ_s/Å, c = 0.8 g/mL
6.9	1.7	6.9	1.7
14.8	1.7		
24.8	1.7	26.9	1.6
34.8	1.4	39.9	1.6
49.8	1.3		
60.0		59.9	1.6
69.8	0.9	69.9	1.5

Table II
Static Screening Length (ξ_s) as a Function of Polystyrene Concentration in Toluene from SAXS at 30 °C

concentration/(g/mL)	ξ_s/Å	concentration/(g/mL)	ξ_s/Å
0.2	11 ± 0.2	0.8	1.4 ± 0.4
0.3	5.3 ± 0.3	0.9	1.8 ± 0.4
0.4	4.0 ± 0.4		

confirm the SANS data correction which has been used. It is suggested that the departure from linear behavior in the concentration dependence at about 0.7 g/mL its due to the proximity to the glassy state and that a limiting value for the screening length is measured at the higher concentrations. This value of ξ_s is only slightly longer than the polystyrene bond length.

Temperature Dependence of the Screening Length. In the semidilute solution range, ξ_s is known to decrease with increasing temperature as the coil swelling increases and leads to more extensive overlap. These results are in accord with expectations that the two-body interactions change linearly with $1/T$.[23] The behavior in the concentrated regime is considerably more complex, particularly

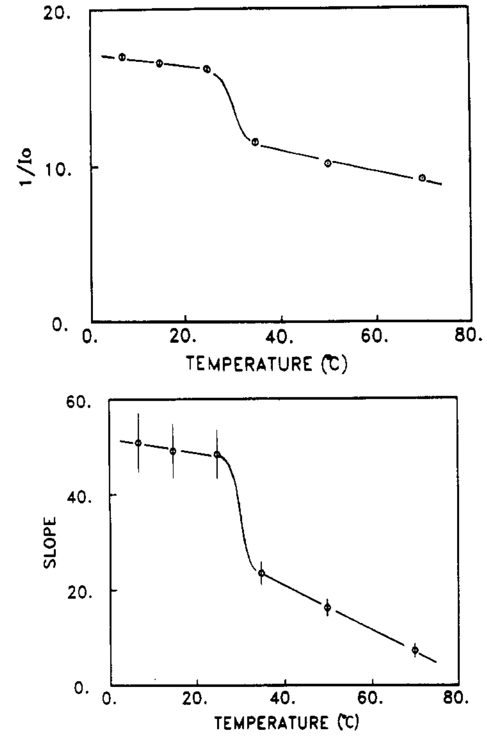

Figure 5. (a) Inverse scattered intensity $I(0)$ from SANS versus temperature for polystyrene concentrations at $c = 0.9$ g/mL. (b) Slopes from the Zimm plots obtained with SANS data as in Figure 2 for the polystyrene concentration 0.9 g/mL.

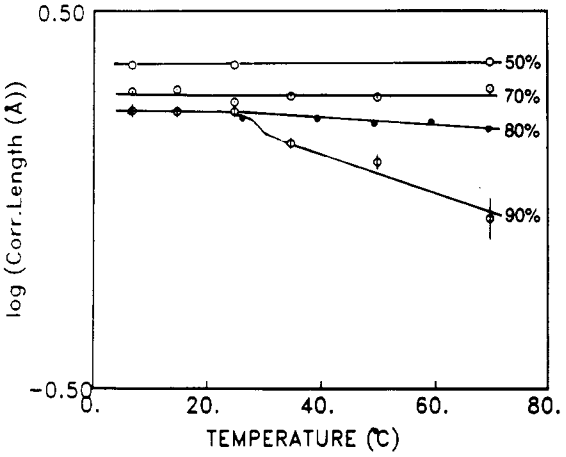

Figure 6. Dependence of log screening length on temperature for different concentrations of polystyrene in deuterated toluene (SANS data).

when the measurements are made in the vicinity of the glass transition. As seen in Figure 5a, a weak temperature dependence of $I(0)$ from the Zimm plots is followed by a strong change at about 30–40 °C. Parallel behavior is observed for the slopes from the Zimm plots depicted in Figure 5b. Figure 6 shows the resulting trends in the screening length, ξ_s.

The glass transition temperature (T_g) for the sample of $C = 0.9$ g/mL was estimated using DSC to lie in the vicinity of 40 °C (and for 0.8 g/mL at 2 °C).[19] These measurements were made with a heating rate of 20 °C/min. The sample of 0.9 g/mL is thus the only one with an "accessible" T_g value. The three points at the lower temperatures for the latter sample correspond to the glassy state, while those at the three higher temperatures lie above T_g; the changes in $I(0)$ with T are attributed to the different isothermal compressibilities above and below T_g (eq 3). Thus at higher temperatures the crosspoint in figure 4 has moved to higher concentrations and a lower value for the screening length.

It may be noted that the decay time distributions obtained by inverse Laplace transformation of dynamic light scattering data[19] show that at the highest concentrations ($C > 0.7$ g/mL), the major component is q independent and it was concluded that it represents the α-relaxation describing segmental relaxations in the PS chain. In the semidilute regime ($C < 0.4$ g/mL) the cooperative diffusion coefficient (D_c) can be used to estimate the dynamic screening length describing hydrodynamic interactions, by means of the relationship

$$\xi_h = kT/6\pi\eta_0 D_c \tag{4}$$

where η_0 is the viscosity of the pure solvent. D_c is given by

$$D_c = \Gamma/q^2(1 - \Phi)^2 \tag{5}$$

Vink has recently[24] discussed the $(1 - \Phi)^2$ factor which assumes great significance above the dilute range.

For a wide range of experimental data in semidilute solutions it was found[12] that the exponent describing the concentration dependence of ξ_h is identical within experimental error to that for ξ_s and the ratio ξ_h/ξ_s is known to equal approximately 2. Muthukumar and Edwards[13] have discussed the relationship between the two screening lengths and predicted a value of the ratio 32/9. With the present data the ratio is also approximately 2 up to a concentration of ≈0.6 g/mL as shown for data summarized in Table I. Beyond this concentration, D_c decreases strongly as the glassy state is approached and local frictional interactions strongly limit diffusional freedom.

Acknowledgment. This work has been supported by the Swedish and the Danish Natural Science Research Councils (NFR and SNF). The authors thank Dr. L. Dvoranek for the synthesis of the polystyrene samples. We thank Dr. C. Konak for discussions during the course of this work.

References and Notes

(1) Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85*, 613; **1966**, *88*, 265.
(2) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, 1986.
(3) Fujita, H. *Polymer Solutions*; Elsevier: Amsterdam, 1990.
(4) (a) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1975**, *37*, 973. (b) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(5) Hamada, F.; Kinugasa, S.; Hayashi, H.; Nakajima, A. *Macromolecules* **1985**, *18*, 2290.
(6) Jannink, G.; de Gennes, P.-G. *J. Chem. Phys.* **1968**, *48*, 2260.
(7) Benoit, H.; Benmouna, M. *Polymer* **1984**, *25*, 1059.
(8) Kinugasa, S.; Hayashi, H.; Hamada, F.; Nakajima, A.; *Macromolecules* **1986**, *19*, 2832.
(9) Geissler, E.; Mallam, S.; Hecht, A.-M.; Rennie, A. R.; Horkay, F. *Macromolecules* **1990**, *23*, 5270.
(10) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(11) King, J. S.; Boyer, W.; Wignall, G. D.; Ullman, R. *Macromolecules* **1985**, *18*, 709.
(12) Brown, W.; Nicolai, T. *Colloid Polym. Sci.* **1990**, *268*, 977.
(13) Muthukumar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.
(14) Brown, W.; Mortensen, K. *Macromolecules* **1988**, *21*, 420.
(15) (a) Koberstein, J. T.; Picot, C. *Polymer* **1986**, *27*, 1595. (b) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 673.
(16) Davidson, N. S.; Richards, R. W.; Maconnachie, A. *Macromolecules* **1986**, *19*, 434.
(17) Schaefer, D. W. *Polymer* **1984**, *25*, 387.
(18) Uhlmann, D. R. *Faraday Discuss.* **1979**, *68*, 87.
(19) Brown, W. M.; Johnsen, R. M.; Konak, C.; Dvoranek, L. *J. Chem. Phys.* **1991**, *95*, 8568.
(20) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093.
(21) Wendorff, J. H.; Fischer, E. W. *Kolloid-Z. Z. Polym.* **1973**, *251*, 876.
(22) Roe, R.-J.; Curro, J. J. *Macromolecules* **1983**, *16*, 428.
(23) des Cloizeaux, J.; Jannink, G.; *Polymers in Solution*; Oxford University Press: Oxford, 1990.
(24) Vink, H. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1725.

Registry No. PS, 9003-53-6; PhMe, 108-88-3.