(12) Gulari, Erd.; Gulari, Es.; Tsunashima, Y.; Chu, B. *Polymer* **1979**, *20*, 347.
(13) Chu, B. *Polym. J.* **1985**, *17*, 225.
(14) Burchard, W. *Chimia* **1985**, *39*, 10.
(15) Vancso, G.; Tomka, I. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*, 116.
(16) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: London, 1971.
(17) Peebles, L. H. *Molecular Weight Distributions in Polymers*; Wiley: New York, 1971.
(18) Davis, P. J.; Rabinowitz, P. *Methods of Numerical Integration*; Academic: New York, 1975; p 327.
(19) Jakeman, E.; Oliver, C. J.; Pike, E. R. *J. Phys. A: Gen. Phys.* **1970**, *3*, 145.
(20) Gut, B.; Tomka, I.; Vancso, G., manuscript in preparation.
(21) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.
(22) Pusey, P. N. In *Industrial Polymers: Characterization by Molecular Weight*; J. H., Green, R., Dietz, Eds.; Transcripta Books: London, 1973.
(23) Pickett, H. E.; Cantow, M. J. R.; Johnson, J. F. *J. Appl. Polym. Sci.* **1966**, *10*, 917.
(24) Vancso, G. *Polym. Bull.* **1986**, *16*, 551.
(25) Tihonov, A. N. *Sov. Math. Dokl. (Engl. Transl.)* **1963**, *4*, 1035, 1624.

Comparison of Correlation Lengths in Semidilute Polystyrene Solutions in Good Solvents by Quasi-Elastic Light Scattering and Small-Angle Neutron Scattering

Wyn Brown*

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

Kell Mortensen

Risø National Laboratory, DK-4000, Roskilde, Denmark. *Received March 31, 1987*

ABSTRACT: Quasi-elastic light scattering (QELS) and small-angle neutron scattering (SANS) experiments have been made on semidilute solutions of polystyrene (PS) in methylene chloride and tetrahydrofuran. The hydrodynamic screening length (ξ_H) from QELS and the excluded volume screening length (ξ) from SANS are found to be proportional at concentrations well above the dilute–semidilute crossover. The power law $C^{-0.68}$ applies to the static quantity whereas this asymptotic exponent value is only found for ξ_H with PS fractions of molecular weight $M \geqslant 10^6$. The dynamic length, ξ_H, is solvent independent while the static length is shown to be significantly shorter in methylene chloride ($\xi_H/\xi = 2.2$ in CH_2Cl_2 and 1.8 in THF), a result which is possibly related to differing extents of coil interpenetration in these solvents.

Introduction

Earlier investigations[1,2] of the dynamical behavior of semidilute solutions of high molecular weight polystyrenes in the good solvent, THF, indicated the presence of bimodal autocorrelation functions in QELS experiments. On theoretical grounds it had been anticipated that a unique correlation length, characterizing the homogeneous transient gel, would be reflected in single-exponential decay. On the other hand, preliminary measurements in another solvent, methylene chloride (CH_2Cl_2), of equivalent solvating power gave the expected narrow line width when using the same samples and with the same measurement parameters. A possible explanation is that there are differences in the extent of coil interpenetration in these solvents. This aspect has recently received attention in neutron scattering experiments[3] and in a novel study using a fluorescence method.[4] These data lend support to the earlier conclusions of Dautzenberg[5] that an overlapping of the internal cores of polymer coils does not occur to the same extent. We note also the similar results given by computer simulations.[6]

A more detailed comparison of the screening lengths of PS in these and other solvents seemed warranted. The possible existence of multiple lengths in semidilute solutions is far from trivial since it calls into question fundamental assumptions on which scaling theory is formulated and which lead to predictions of the universality of solution behavior.

From the notation of Edwards,[7,8] ξ and ξ_H are respectively the screening lengths for the excluded-volume and hydrodynamic interactions. The excluded-volume effect is a static quantity which in semidilute solutions is accessible to measurement by using small-angle neutron scattering (SANS) or small-angle X-ray scattering (SAXS). The dynamic quantity may be obtained by using QELS or with samples of lower molecular weight by using the neutron spin–echo technique. Past studies have emphasized the testing of the power law predictions for the concentration dependence of the correlation length (or cooperative diffusion coefficient). According to scaling theory,[9] ξ is related to the concentration, C, by

$$\xi \sim C^{-\nu/(3\nu-1)} \tag{1}$$

where ν is the excluded-volume exponent in the relationship $R_g \sim M^\nu$ (where R_g is the gyration radius and M molecular weight). For good solvents, $\nu = 0.6$ in the limit of infinite M, which leads to a concentration exponent of -0.75 in eq 1. However, numerous experimental investigations (see, for example, ref 1 and 10–15) have established a value of about -0.67 for both ξ and ξ_H.

Differences in the absolute values of ξ and ξ_H and their ratio have received less attention. These quantities were implied by de Gennes[9] to be identical whereas Muthukumar and Edwards[8] stress the essential physical difference between them.

This paper is directed partly to an examination of the behavior of PS in CH_2Cl_2 in greater detail than hitherto and partly to a comparison of the screening lengths in this solvent and THF. Both QELS and SANS measurements have been made over the semidilute regime on essentially monodisperse PS fractions.

Experimental Section

Polystyrene samples (PSH) and deuteriated polystyrene (PSD) with the same molecular weight (1.01×10^5) were obtained

0024-9297/88/2221-0420$01.50/0

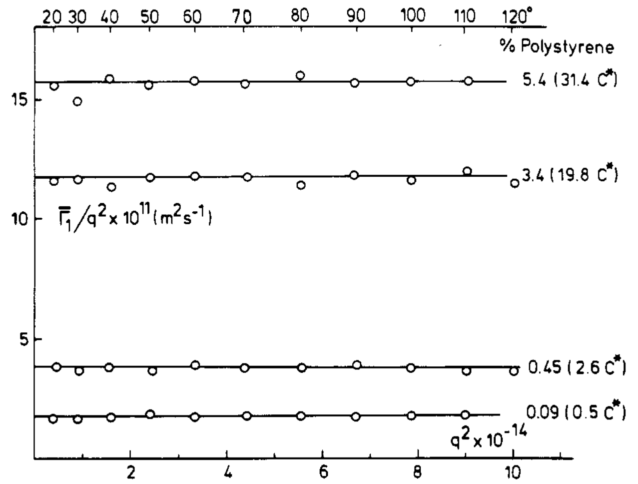

Figure 1. QELS data. Effective diffusion coefficient ($\bar{\Gamma}_1/q^2$) as a function of the scattering vector (q^2) for polystyrene ($\bar{M}_w = 2.95 \times 10^6$) in methylene chloride at a series of semidilute concentrations ($C^* = [\eta]^{-1}$).

from Polymer Laboratories, Shrewsbury, U.K. These samples were essentially monodisperse ($\bar{M}_w/\bar{M}_n = 1.03$). The fractions with $\bar{M}_w = 9.3 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 1.04$ and $\bar{M}_w = 2.95 \times 10^6$ and $\bar{M}_w/\bar{M}_n = 1.06$ were obtained from Toya Soda Ltd., Tokyo. Solutions were prepared in glass vials, sealed at −15 °C, and these slowly rotated for several weeks. (It was observed that solutions in methylene chloride that were allowed to stand for a period of more than 6 months became slightly yellow.)

Quasi-elastic light scattering (QELS) measurements were made on solutions of PSH using the apparatus and techniques earlier described. Dilute solutions ($<C^*$) were slowly filtered (two passes) through a 0.22-μm Fluoropore filter into 10 mm precision-bore NMR tubes (Wilmad Glass Ltd., NJ). The solutions were essentially dust free as far as could be ascertained by using signal stability as the criterion. Higher concentrations were prepared by very slow evaporation of solvent from the tubes in a dust-free atmosphere. The concentration range was thus extended from the very dilute up to about 10 g/100 mL, as shown in Figure 2.

Small-angle neutron scattering (SANS) experiments were performed by using the facility at Risø, Denmark. The cold source of the 10-MW research reactor DR3 was used. Thermal neutrons are available in the range $2.5 < \lambda < 30$ Å and the wavelength could be defined with a mechanical velocity selector. In the present experiments, λ of 3.66 and 10.12 Å were used in the methylene chloride system. The latter wavelength was included to check the validity of the data at even smaller scattering angles.

In the case of the THF solutions the wavelength was 5.13 Å. The scattered radiation was monitored on a two-dimensional He^3 detector with a sensitive area of diameter 59 cm. The whole area was divided into 64 × 64 channels. The sample–detector distance was 3.0 m. After subtraction of the blank scattering, all data were normalized to the incoherent scattering of a polyethylene "lupolene" sample. The solutions (hydrogenated solvents) were contained in 1-mm pathlength quartz cells (Hellma, FRG), equipped with special spring-loaded Teflon stoppers and O-ring seals to prevent evaporation of the low boiling point solvents used in this study. The scattering vector range ($q = (4\pi/\lambda) \sin(\theta/2)$) was between 0.008 and 0.1 $Å^{-1}$.

All solvents were spectroscopic grade (Merck, Darmstadt, FRG). They were dried over freshly treated (350 °C, high vacuum) molecular sieves (3 Å, Union Carbide), as described earlier.[1,2] The earlier measurements of dynamic light scattering had revealed the presence of a slow relaxation which was eliminated by the above drying procedure.

The measurements were made at 25 °C unless otherwise stated.

Results and Discussion

Quasi-Elastic Light Scattering. QELS measurements were made on PS fractions of different molecular weights as a function of both scattering vector (q) and concentration in CH_2Cl_2. The autocorrelation functions approximated single exponentials (normalized second cumulant ≤0.05). The quantity $\bar{\Gamma}_1/q^2$, where Γ_1 is the initial decay rate of concentration fluctuations, was found to be independent of q over a wide range as shown for typical data on $\bar{M}_w = 3 \times 10^6$ in Figure 1. This establishes diffusive motion, ($D = \bar{\Gamma}_1/q^2$). Figure 2 gives log–log plots of the effective diffusion coefficient vs concentration where the latter spans the dilute–semidilute regions. There is a pronounced transition between these regimes. It is noted that the inverse intrinsic viscosity ($[\eta]^{-1}$) provides a useful measure of the overlap concentration (C^*). Alternative measures of the latter are summarized in Table I; recent discussions of C^* are those of Wells[16] and Ying and Chu.[17]

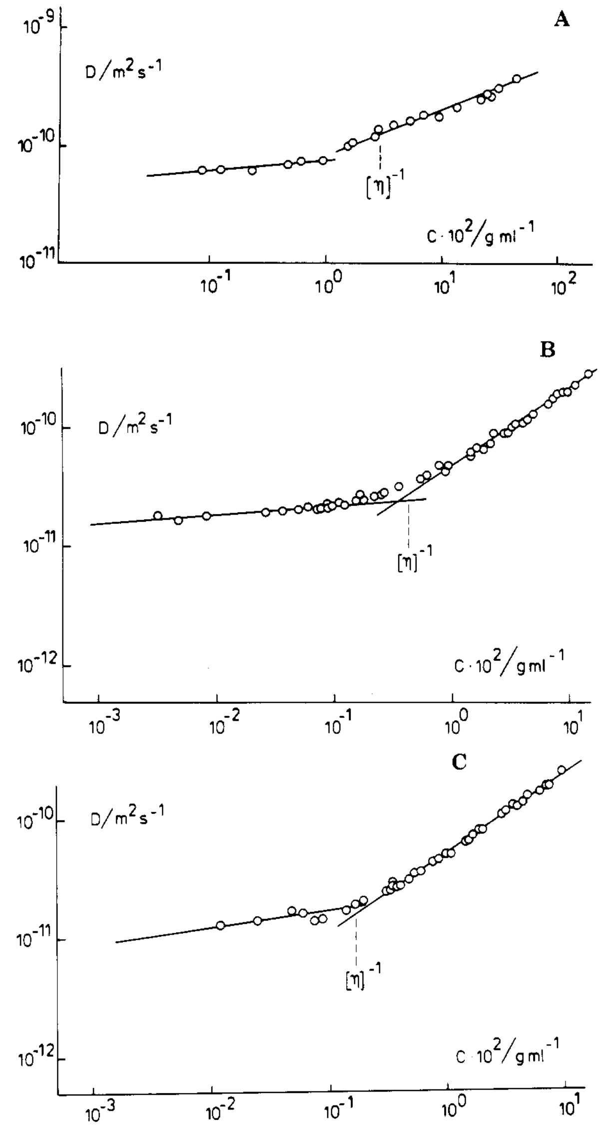

Figure 2. QELS data. Typical log–log plots of the diffusion coefficient (cumulants evaluation) as a function of concentration of polystyrene in methylene chloride. Data at 25 °C. Values of $[\eta]^{-1}$ are inserted as a measure of C^*. Molecular weights: (A) 1×10^5; (B) 9.3×10^5; (C) 2.95×10^6. The slopes in the semidilute ranges are, respectively, 0.56, 0.68, and 0.68.

Table I
Estimated Values of the Overlap Concentration ($C^* \times 10^2$/g•mL^{-1})

	$\bar{M}_w = 2.95 \times 10^6$	$\bar{M}_w = 9.3 \times 10^5$	$\bar{M}_w = 1 \times 10^5$
exptl	0.23	0.40	1.7
$[\eta]^{-1}$	0.17	0.42	2.3
$3M/\pi R_g^3 N_A$	0.11	0.3	1.64
$M/R_g^3 N_A$	0.46	1.26	6.9

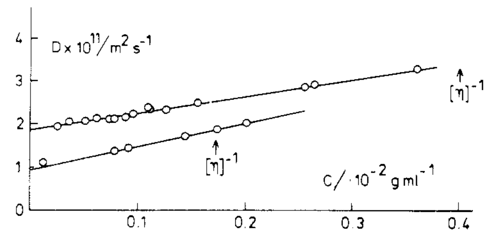

Figure 3. QELS data. Extrapolation of diffusion coefficients to infinite dilution. The upper line gives data in methylene chloride for fraction B (M_w 9.3 × 10^5) and the lower for fraction C ($\bar{M}_w$ = 2.95 × 10^6). Values of $[\eta]^{-1}$ are inserted as a measure of $C*$.

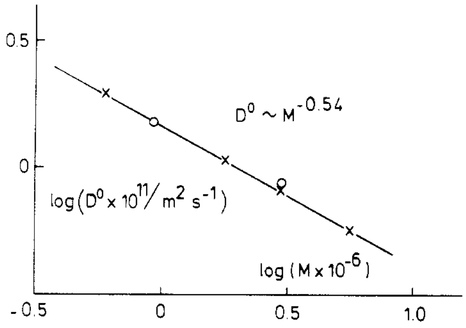

Figure 4. Comparison of extrapolated D^0 values in methylene chloride as obtained from Figure 3 with data from ref 19 for polystyrene in tetrahydrofuran at 30 °C in a plot of log D^0 versus log M.

The curves for the two higher molecular weights are superimposable in the semidilute region, demonstrating the expected molecular weight independence of the cooperative diffusion coefficient. The corresponding slope corresponds to the exponent γ = 0.68, which is in good agreement with a number of literature reports[10-15] for good-solvent systems. The slope for the lowest molecular weight ($\bar{M}_w = 10^5$) is lower (γ = 0.56), which is also typical for the nonasymptotic behavior of flexible coils of low M in D versus C plots—see the review by Nyström and Roots,[18] for example.

The dilute solution data have been extrapolated to infinite dilution (Figure 3) to obtain values of D^0. D^0 values in the solvents CH_2Cl_2 and THF[19] are similar in magnitude (Figure 4). Note that the solvent viscosities are also similar ($\eta_{THF}{}^{30}$ = 0.428 cP and $\eta_{CH_2Cl_2}{}^{25}$ = 0.423 cP).[20]

Since the intrinsic viscosities[21] show the same behavior (Figure 5), one may conclude that the two solvents are comparable in solvating power/draining behavior.

Dynamic correlation lengths (ξ_H) have been evaluated at each concentration from the effective diffusion coefficients by using the Stokes-Einstein equation

$$\xi_H = kT/6\pi\eta_0 D \tag{2}$$

where the symbols have their usual significance, η_0 being the viscosity of the pure solvent. In all cases, the D values from which ξ_H have been calculated refer to values corrected to the solvent frame of reference by dividing by the factor $(1 - \varnothing_p)$ where $\varnothing_p$ is the volume fraction of PS. Values of ξ_H are shown in log–log plots as a function of concentration (Figure 6). Data are included for the same samples measured in THF, the investigation of which was the subject of earlier papers.[1,2] In order to be consistent with the form of data treatment used in the CH_2Cl_2 system, and also to facilitate comparison with the time-averaged correlation length (ξ) from SANS measurements (see below), the D values are those estimated by the method of cumulants (ref 37). The slopes of the lines are −0.68 (Figure 6A) and −0.56 (Figure 6B). The data are in both diagrams well represented by a common line in the two solvents.

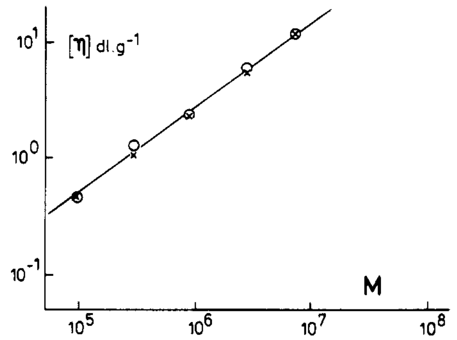

Figure 5. Intrinsic viscosity versus molecular weight in a log–log plot for polystyrene in methylene chloride (○) and corresponding data in tetrahydrofuran (×) taken from ref 21. The equation $[\eta] = 1.1 \times 10^{-2}\, M_w{}^{0.72}$ represents the methylene chloride data.

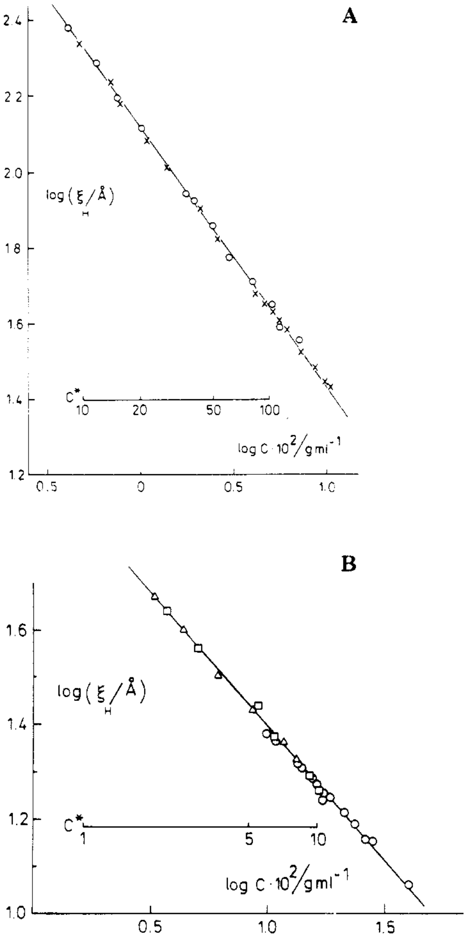

Figure 6. (A) Log–log plots of the dynamic correlation length (ξ_H) versus concentration by QELS measurements for polystyrene ($\bar{M}_w$ = 2.95 × 10^6) in methylene chloride (○) and tetrahydrofuran (×). $C*$ estimated as $[\eta]^{-1}$. Equation of the line: $\xi_H = 5.7C^{-0.68}$. (B) Plot analogous to (A) for $\bar{M}_w$ = 1 × 10^5. Data for methylene chloride (○), tetrahydrofuran (△), and benzene (□). Equation of the line: $\xi_H = 2.5C^{-0.56}$.

It has been assumed here that the monomeric friction coefficient is essentially constant with concentration. This is approximately true up to a concentration of about 15%,[22,23] which is the highest concentration in Figure 6A. In Figure 6B the concentration range exceeds this value, but the points do not indicate a systematic departure from the power law followed in the lower concentration interval.

As mentioned in the Introduction, bimodal analysis of the data for the PS/THF system gave a gel mode (fast mode) exponent of −0.57, together with a slower (transla-

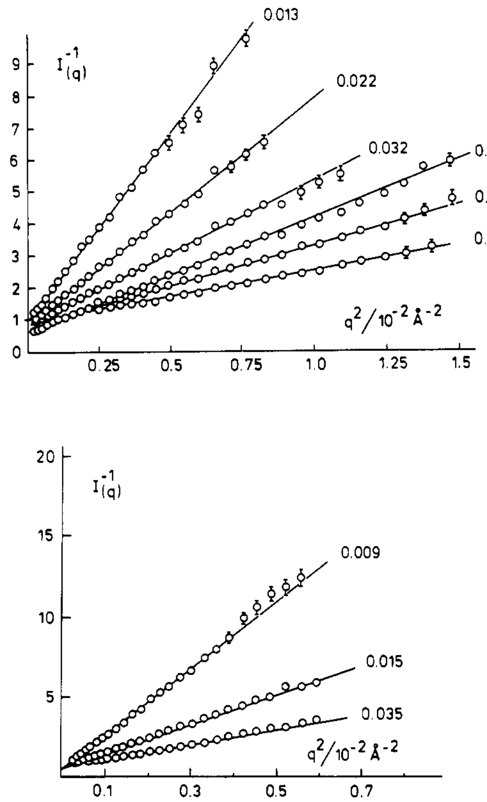

Figure 7. (Top) Typical SANS data for polystyrene ($\bar{M}_w = 1 \times 10^5$) in methylene chloride at the concentrations (volume fraction, ϕ) indicated. The ratio (slope/intercept) gives ξ^2 according to eq 3. The data were collected at $\lambda = 3.66$ Å at 25 °C. Confidence intervals (95%) lie within the size of the point unless otherwise indicated. (Bottom) Plots analogous to those above for the same polystyrene fraction but dissolved in tetrahydrofuran. Data collected at $\lambda = 5.13$ Å and 25 °C. Concentrations are in volume fraction (ϕ) as indicated.

tional) mode with an exponent of -0.44.[1,2] Amis and Han[24] have also used a bimodal model to treat their data for semidilute solutions of PS in THF. Their fast mode was characterized by a fast mode (exponent -0.50) together with a slow mode having a strong dependence on concentration but of opposite sign, which may derive from the presence of clusters of chains.

Small-Angle Neutron Scattering. SANS measurements have been made on semidilute solutions of PS ($\bar{M}_w = 1 \times 10^5$) in the deuteriated form dissolved in the hydrogenated solvents CH_2Cl_2 and THF. This molecular weight was used since it was the highest then available with identical molecular weights for the hydrogenated and deuteriated forms of PS. These were required for a parallel study of the single chain radius of gyration in different solvents using the high concentration technique as recently employed by King et al.[25] for PS in toluene.

Experiments were made at two wavelengths in CH_2Cl_2 (3.6 and 10 Å) and the evaluated correlation lengths found to be the same within experimental error. Measurements were subsequently made in THF at a wavelength of 5.1 Å.

The static structure factor, S_q, is given in terms of the correlation length and the scattering vector, q, by the Lorentzian scattering law:

$$S_q = f_{T,C}/(q^2 + \xi^{-2}) \qquad (3)$$

Utilization of the Lorentzian broadening in the q-region corresponding to $q\xi \leq 1$ yields ξ^2 as the ratio of the slope to intercept in linear plots of the reciprocal intensity (I_q^{-1}) versus q^2. Such plots are illustrated in Figure 7. (One may also use the extrapolated intercept to obtain ξ^{-2} but this approach[26] seems to be complicated by deviations from linearity due to an increase in scattered intensity at low q values as recently discussed by Koberstein et al.[27]) Table II summarizes values of ξ as a function of concentration. A log–log plot of ξ versus C is shown in Figure 8. Data of King et al.[25] are included and refer to PS of the same molecular weight but in toluene as solvent. Although other neutron scattering data exist for PS in good solvents (e.g., in carbon disulfide[28] and benzene[29]) these display inordinate scatter. Thus with the exception of the data of King et al.,[25] there is a dearth of reliable values of the correlation length as a function of concentration for PS in good solvents. Hamada et al.[30] and Yukioka et al.[31] report data for the correlation length of PS in toluene determined by using small-angle X-ray scattering (SAXS). These were completely compatible with those from complementary measurements by static light scattering at low q and also agree numerically with values of ξ determined by King et al.[25]

Table II
Correlation Lengths from SANS Measurements[a]

methylene chloride			tetrahydrofuran		
ϕ	$C \times 10^2$/g·mL^{-1}	ξ/Å	ϕ	$C \times 10^2$/g·mL^{-1}	ξ/Å
0.0044	0.46	46.9	0.015	1.61	39.7
0.0088	0.92	38.9	0.025	2.58	32.9
0.013	1.36	34.7	0.035	3.64	28.1
0.022	2.33	28.6	0.049	5.09	22.1
0.028	2.96	25.6	0.059	6.20	19.6
0.032	3.33	23.4	0.075	7.82	15.6
0.051	5.37	17.0	0.126	13.2	10.8
0.077	8.10	12.7			
0.11	11.55	10.2			
0.144	14.82	9.3			

[a] Values of the static correlation length (ξ). Semidilute solutions of polystyrene ($\bar{M}_w = 1 \times 10^5$) in methylene chloride and tetrahydrofuran. Concentrations in volume fraction (ϕ) and C (g·mL^{-1}).

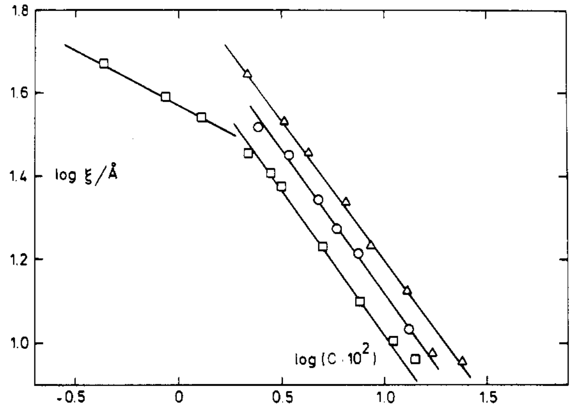

Figure 8. Log–log plots of the static correlation length (ξ) as a function of polystyrene concentration (C, g·mL^{-1}) derived from plots such as those in Figure 7 (according to eq 3). The data are for $\bar{M}_w = 1 \times 10^5$ in methylene chloride (□), tetrahydrofuran (○), and toluene (△)—taken from ref 25. The slopes in the semidilute region are -0.68 in CH_2Cl_2 and THF and -0.70 in toluene. In the dilute region (data in CH_2Cl_2) $\xi = (R_g/3^{1/2})_{c\rightarrow 0}$ where R_g is the radius of gyration.

In methylene chloride there is a distinct break between the dilute and semidilute concentration regimes, which is again situated at approximately $[\eta]^{-1}$ as found with the QELS data. The apparent value of ξ determined in the dilute region is given by $\xi = R_g/3^{1/2}$, although this interpretation is ambiguous in the vicinity of C^*. Rather, $\xi \rightarrow R_g/3^{1/2}$ as $C \rightarrow 0$.[14]

The dilute solution data in THF were unduly scattered and are thus omitted here since the present discussion only concerns the semidilute region. While the slopes of the

Table III
Comparison of Static and Dynamic Correlation Lengths[a]

solvent	ξ_H(QELS)/Å	ξ(SANS)/Å	ξ_H/ξ
methylene chloride	25.2	11.5	2.2
tetrahydrofuran	25.5	14.5	1.8
toluene[25]	32.5	15.5	2.1

[a] From QELS (ξ_H) and SANS (ξ) measurements for polystyrene ($\bar{M}_w = 1 \times 10^5$) at a concentration of $C = 0.1$ g·mL^{-1} in different solvents.

log–log plots in Figure 8 are the same within experimental uncertainty ($\sim C^{-0.68}$), the correlation lengths at a given concentration differ substantially. The following relationships apply: $\xi = 2.2C^{-0.68}$ (CH_2Cl_2); $\xi = 2.7C^{-0.68}$ (THF); $\xi = 3.1C^{-0.7}$ (toluene[25]). The coefficient for toluene is similar to that for PS in benzene (data of Cotton et al.[29]). Since our SANS measurements in CH_2Cl_2 and THF were made on two occasions 5 months apart, the reproducibility was checked by repeating measurements of ξ on the second occasion in CH_2Cl_2. These fell on the same line as the earlier determined values.

SANS experiments were also made on semidilute (C = 3.1%) solutions of PS ($M = 10^5$) in CH_2Cl_2 over the temperature range −10 to +40 °C; ξ did not change significantly within this range.

Davidson et al.[32] have demonstrated the influence of solvent quality by measurements of ξ using SANS on PS gels in cyclohexane at temperatures above the Θ-point. It was observed that the difference between ξ and ξ_H (from QELS) decreases with improving solvent quality (i.e., increasing temperature).

The smaller value of the screening length found in CH_2Cl_2 at a given concentration compared with that in THF at the same value would suggest a larger excluded volume effect in the former solvent. This difference contrasts with the solvent independence of ξ_H from QELS measurements. A contributory seat of the difference could lie in different extents of coil interpenetration as discussed in the Introduction. The bimodality of the correlation functions in THF and the single modal relaxation pattern in CH_2Cl_2 suggests possible differences in solution structure over the same concentration range.

In order to compare static and dynamic lengths, we have arbitrarily selected a concentration of $C = 0.1$ g·mL^{-1}, since at this concentration one may safely assume that C^* is comfortably exceeded in good solvents even at a molecular weight of 10^5. Values of ξ and ξ_H at this concentration are listed in Table III. The ratio ξ_H/ξ is about 2 in these good solvents which may be compared to the value of 32/9 given by Muthukumar and Edwards.[8] de Gennes[9] implies, on the other hand, that the two lengths are identical. There is of course considerable uncertainty in the evaluation of these characteristic lengths from very different experimental techniques and calculation procedures. Nevertheless, the accumulated evidence supports the statement in ref 8 that ξ and ξ_H are screening lengths having physically very different origins. We draw attention to a subtle difference in the static and dynamic lengths in crossover behavior. While the static length is related to the concentration through the asymptotic value of the exponent ($C^{-0.68}$) above C^* even for samples of modest molecular weight (e.g., $M = 10^5$), the dynamic quantity is described by this exponent only for fractions of substantially higher M (e.g., $\xi_H \sim C^{-0.56}$ for $M = 10^5$ but $C^{-0.68}$ for $M = 9.3 \times 10^5$ and 3×10^6). This behavior is related[33] to the determination of an inverse distance in measurements of the dynamic property whereas $\langle r^2 \rangle$ is determined in the static experiment, which places different emphasis on crossover effects.

Wiltzius et al.[13] have measured ξ_H using QELS on PS samples of various molecular weight in toluene in the semidilute region. These data were compared with values of ξ previously determined[14] by using static light scattering, although in this case the concentration range was restricted to the dilute/semidilute crossover region where it is still possible to estimate ξ at the wavelength used in light scattering. Not surprisingly, they then found the ratio ξ_H/ξ to be concentration dependent, although a value of the ratio of about 2 is approached at $C \cong 0.01$ g·mL^{-1} in agreement with the figures in Table III. Similar nonasymptotic behavior is exhibited by the results of Coviello et al.[34] for the stiff-chain polymer xanthan in aqueous solution (for which the exponent relating the diffusion coefficient to concentration is approximately 0.6 and thus limiting scaling behavior has not been attained). Whereas a high molecular weight native xanthan sample shows a constant value of $\xi_H/\xi \cong 1.7$, pyruvate-free and acetate-free samples of lower M were characterized by a concentration-dependent ratio of the lengths, although a trend to an asymptotic value of about 2.8 can be discerned.

We conclude, consequently, that when a concentration dependence of the ratio ξ_H/ξ is observed it probably reflects residual crossover effects. This is a nontrivial aspect since scaling behavior requires at least that the two lengths are proportional.

Ewen et al.[34] have attempted to measure ξ_H using the neutron spin–echo technique. Although they drew the conclusion that the values of ξ_H were of similar magnitude to those for ξ previously determined by SANS, the data were insufficient to permit determination of the power law for ξ_H.

It may also be noted that Numasawa et al.[36] find $\xi_H/\xi = 4\nu$ (i.e., $\cong 2.3$) where ν is the excluded-volume exponent, from a discussion of the onset of entanglement behavior. The present results, summarized in Table III, confirm a proportionality between ξ_H and ξ, with a constant of about 2 when the measured concentration range extends well into the semidilute region. The accumulated results cast some doubt on the universality of scaling behavior but further discussion is reserved for a future contribution dealing with a comparison of single-chain radii determined by SANS.

Acknowledgment. We are grateful to the Swedish Natural Science Research Council for financial support and for assistance by providing the facilities at Risø National Laboratories, Roskilde, Denmark. Our thanks are also due to Drs. Robert Ullman and Randal Richards for advice during this study. The assistance of David Holland with the quasi-elastic light scattering measurements on polystyrene in methylene chloride is hereby acknowledged.

Registry No. PS, 9003-53-6; neutron, 12586-31-1.

References and Notes

(1) (a) Brown, W. *Macromolecules* **1985**, *18*, 1713; **1986**, *19*, 2002. (b) Brown, W.; Johnsen, R. M. *Macromolecules* **1985**, *18*, 379.
(2) Brown, W. *Macromolecules* **1986**, *19*, 1083.
(3) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 673.
(4) Chang, L. P.; Morawetz, H. *Macromolecules* **1987**, *20*, 428.
(5) Dautzenberg, H. *J. Polym. Sci., Polym. Symp.* **1977**, *61*, 83.
(6) Olaj, O. F.; Pelinka, K. H. *Makromol. Chem.* **1976**, *177*, 3413.
(7) Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85*, 613; **1966**, *88*, 265.
(8) Muthukumar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.
(9) de Gennes, P.-G. In *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979.
(10) Adam, M.; Delsanti, M. *Macromolecules*, **1977**, *10*, 1229.
(11) Richter, D.; Ewen, B.; Hayter, J. B. *Phys. Rev. Lett.* **1980**, *45*, 2121.
(12) Ewen, B.; Richter, D.; Hayuter, J. B.; Lehnen, B. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 233.
(13) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1984**, *53*, 834.

Macromolecules **1988,** *21,* 425–432

(14) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1983,** *51,* 1183.
(15) Štěpánek, P.; Koňák, Č. *Adv. Colloid Interface Sci.* **1984,** *21,* 195.
(16) Wells, J. F. *J. Chem. Soc., Faraday Trans. 1* **1984,** *180,* 1233.
(17) Ying, Q.; Chu, B. *Macromolecules* **1987,** *20,* 362.
(18) Nyström, B.; Roots, J. *J. Macromol. Sci.—Rev. Macromol. Chem.* **1980,** *C19* (1), 35.
(19) Jamieson, A. M.; Venkataswamy, K. *Polym. Bull.* **1984,** *12,* 275.
(20) Landholt-Börnstein, Springer Verlag, 1979; Vol. 5.
(21) Meyerhoff, G.; Appelt, B. *Macromolecules* **1979,** *12,* 968.
(22) von Meerwall, E. D.; Amis, E. J.; Ferry, J. D. *Macromolecules* **1985,** *18,* 260.
(23) Kim, H.; Chang, T.; Yohanan, J. M.; Wang, L.; Yu, H. *Macromolecules* **1986,** *19,* 2737.
(24) Amis, E. J.; Han, C. C. *Polymer* **1982,** *23,* 1403.
(25) King, J. S.; Boyer, W.; Wignall, J. D.; Ullman, R. *Macromolecules* **1985,** *18,* 709.
(26) Cotton, J. P.; Nierlich, M.; Boué, F.; Daoud, M.; Farnoux, B.; Jannink, G.; Duplessix, R.; Picot, C. *J. Chem. Phys.* **1976,** *65,* 1101.
(27) Koberstein, J. T.; Picot, C. *Polymer* **1986,** *27,* 1595.
(28) 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.
(29) Cotton, J. P.; Farnoux, B.; Jannink, G. *J. Chem. Phys.* **1972,** *57,* 290.
(30) Hamada, F.; Kinugasa, S.; Hayashi, H.; Nakajima, A. *Macromolecules* **1985,** *18,* 2290.
(31) Yukioka, S.; Higo, Y.; Noda, I.; Nagasawa, M. *Polym. J.* **1986,** *18,* 941.
(32) Davidson, N. S.; Richards, R. W.; Maconnachie, A. *Macromolecules* **1986,** *19,* 434.
(33) Daoud, M.; Jannink, G. *J. Phys. Lett.* **1980,** *41,* 217.
(34) Coviello, T.; Burchard, W.; Dentini, M.; Crescenzi, V. *Macromolecules* **1987,** *20,* 1102.
(35) Ewen, B.; Stuhn, B.; Binder, K.; Richter, D.; Hayter, J. B. *Polym. Commun.* **1984,** *25,* 133.
(36) Numasawa, N.; Kuwamoto, K.; Nose, T. *Macromolecules* **1986,** *19,* 2593.
(37) Koppel, D. E. *J. Chem. Phys.* **1972,** *57,* 4814.

Temperature and Concentration Dependence of the Interaction Parameter in Oligomeric Polymer Blends from Small-Angle Neutron Scattering and Calorimetric Measurements

P. E. Tomlins and J. S. Higgins*

Department of Chemical Engineering, Imperial College, London SW7 2BY, United Kingdom. *Received December 1, 1986*

ABSTRACT: Small-angle neutron scattering has been used to determine the concentration and temperature dependence of the interaction parameter χ in a blend of two polymers. The interaction parameter can be obtained either by analyzing the angular dependence of the scattering in terms of an apparent radius of gyration or by extrapolation of the data to zero scattering angle. We present here a comparison of these two methods for two blends of oligomeric polystyrene with polybutadiene. One blend containing labeled (deuteriated) polystyrene with hydrogenous polybutadiene and the other deuteriated polybutadiene with hydrogenous polystyrene. The temperature dependence of the interaction parameter has also been determined for a blend of oligomeric methoxylated poly(ethylene glycol) with methoxylated poly(propylene glycol) where the latter component contains a percentage of labeled chains. The availability of heat of mixing data for these systems has also enabled us to assess in part the enthalpic and entropic contributions to the interaction parameter.

1. Introduction

In several recent papers[1-6] it has been shown that small-angle neutron scattering measurements from a single-phase two-component polymer blend containing concentration fluctuations may be used to determine the Flory–Huggins interaction parameter. The concentration fluctuations in such a system were originally shown by Einstein[7] to depend on the concentration gradient of the chemical potential which Debye and Bueche[8] subsequently related to interactions in the system using the Flory-Huggins equation.[9]

In the first neutron scattering papers on this subject[2,4] only the intensity of the scattering extrapolated to zero angle was analyzed in order to obtain the interaction parameter. However, in a recent publication, Benoit et al.[6] have argued that a more precise value of the interaction parameter can be obtained by analyzing the angular dependence of the scattering in terms of an apparent radius of gyration. Shibayama[5] et al have also analyzed their scattering data as a function of angle using a complex nonlinear regression in order to obtain both the interaction parameter and a correlation length for the fluctuations.

In this paper we have analyzed the concentration fluctuations in low molecular weight blends of polystyrene with polybutadiene and of methoxylated poly(propylene glycol) with methoxylated poly(ethylene glycol) using small angle neutron scattering. These blends show upper critical solution temperatures,[10-12] and by labeling one or other component by deuteriation the intense scattering resulting from concentration fluctuations may be observed in the single-phase region at elevated temperatures. We have extracted the interaction parameters as a function of temperature and concentration by systematically analyzing both the intensity extrapolated to zero angle and the apparent radius of gyration following the Benoit method. This allows us to compare the two approaches and to explore the sensitivity of the analyses to the molecular parameters required for their application. The values of the interaction parameters are then compared with the functional dependences predicted by current thermodynamic theories. In some cases values of the enthalpy of mixing are available for similar systems and correlation of these data with the neutron results allows the entropic and enthalpic contributions to the interaction parameter to be assessed in more detail.

2. Small-Angle Scattering from Binary Blends

The scattering from a binary blend composed of polymers 1 and 2 has been shown to be given by[1]

$$S(Q) = \frac{(cd + (1-c)h - b')^2}{P_1^{-1}(Q) + \beta P_2^{-1}(Q) - 2\beta U} + c(1-c)(d-h)^2 P_1(Q) \quad (1)$$

where polymer 1 contains a fraction c of chains labeled by

0024-9297/88/2221-0425$01.50/0