Scattering by Modestly Concentrated Polymer Solutions

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ABSTRACT: The angular dependence of static scattering intensity for polymer solutions beyond coil overlap is commonly associated with excluded-volume screening behavior. This interpretation is supported by the power-law concentration dependence for sizes obtained with an Ornstein−Zernike analysis and agreement with the predicted exponents for screening length. However, the data supporting these power laws continue unabated to concentrations well beyond the range of significant volume exclusion, yielding physically unrealistic lengths and suggesting some fundamental flaw in the screening interpretation. An alternative, nonscreening interpretation is offered in this paper. It is based on the de Gennes equation, already widely used for determining chain dimensions and interaction strength in polymer blends. It is applied here, seemingly for the first time, to the scattering from solutions of polymers in both good and Θ solvents. It accounts reasonably well, without freely adjustable parameters, for published data on several systems and eliminates the apparent anomalies that a screening interpretation introduces. The analysis seems able to provide two quantities not easily obtained at modest concentrations, a size measure for the unperturbed polymer, $R_g{}^2/M$, and the polymer−solvent interaction parameter, χ.

Introduction

How chain dimensions vary with concentration is an interesting question in its own right, but it is also essential information for understanding the concentration dependence of polymer solution dynamics. Small-angle neutron scattering (SANS) measurements can unambiguously answer the question, but inconsistency among results from relatively few such studies has left it currently unsettled. There is also pertinent information from related SANS investigations of excluded-volume screening lengths, but it confounds rather than helps to resolve the chain dimensions inconsistency. Results of the screening length studies agree: the data for both good and Θ solutions obey power laws with exponents essentially as predicted by screening and scaling arguments. However, the data and power laws describing them continue into the high concentration regime, well beyond the expected ranges, and they yield sizes that are too small to be seriously regarded as screening lengths. Here we propose a nonscreening interpretation of scattering-derived microscopic lengths in solutions that would seem at least to simplify and make the situation on chain dimensions clearer.

Background

The variation of polymer chain dimensions with concentration for polymers in good solvents is not a settled matter. Determination of radius of gyration R_g as a function of polymer volume fraction ϕ requires small-angle neutron scattering (SANS) data for solutions containing mixtures of protonated and deuterated chains. The experiments are technically demanding as well as time-consuming, and only three SANS-based studies have been conducted.[1−3] Even for those, the available q range was such that only chains of relatively small size could be used, $R_g \lesssim 15$ nm, with a correspondingly small difference between size in the dilute limit $R_g(0)$ and in the melt $R_g(1) \sim (R_g)_\theta$. Polystyrene solutions were used in the first two studies,[1,2] and in each a single power-law relationship was reported for $R_g(\phi)$ through the entire range, from coil overlap $\phi \sim \phi^*$ to $\phi = 1$. A third study[3] was conducted recently by Westermann et al. with solutions of a model polyethylene in nonadecane for the range $0.25 \leq \phi \leq 1$. In this case, no significant change in R_g was found: $R_g(\phi) \approx R_g(1)$ over the entire range. Westermann et al. went on to note that the values of R_g at high concentrations reported in the first of the two earlier studies were probably incorrect, the reported sizes being significantly smaller than the now known values for their molecular weights in the melt state. Accordingly, the conclusion of that polystyrene study—R_g varies by a single power law over the entire range of concentrations—is probably invalid. Results from the Westermann et al. study indicate that $\phi^\ddagger$, the concentration beyond which R_g has essentially reached $R_g(1) \sim (R_g)_\theta$, is less than 0.25.

A screening-based estimate of $\phi^\ddagger$ can be obtained from dilute solution data in both good and Θ solvents.[4] Briefly, $\phi^\ddagger$ is obtained from $M^\ddagger$, the molecular weight at which R_g and $(R_g)_\theta$ merge ($R_g \sim (R_g)_\theta$ for $M \lesssim M^\ddagger$). The concentration at which the excluded-volume screening length ξ_{ev} reaches $R_g{}^\ddagger$ is $\phi^\ddagger$. The range $\phi^\ddagger \sim 0.1$ is suggested by the data for many good solvent systems,[5] a crossover concentration that is of course consistent with the Westermann et al. data. The correlation length ξ from another type of SANS experiment, when interpreted as if it were ξ_{ev}, suggests a seemingly contrary conclusion, that size-related changes continue to occur at the microscopic level over the entire range of concentrations.

Fits to the Ornstein−Zernike expression are used to extract the correlation length from an observed angular dependence of coherent SANS intensity:

$$I(q,\phi) = \frac{I(0,\phi)}{1 + q^2\xi^2} \tag{1}$$

where $q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector, with λ the neutron wavelength and θ the scattering angle. Intensity varies with q over a wide

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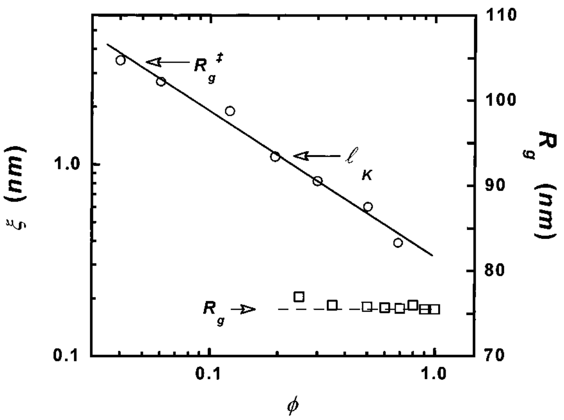

Figure 1. Comparison of correlation length and radius of gyration for polyethylene in linear alkane solvents. The open circles (○) denote correlation lengths[7] and the open squares (□) radii of gyration.[3] The solid line is the power law given as eq 3; values of $R_g^\ddagger$ and l_K estimated from polyethylene size data in good and Θ solvents.

range of concentrations, and ξ is obtained at each concentration from the ratio of slope to intercept in a plot of $1/I(q)$ vs q^2.

Equation 1 seems to describe the experimental scattering data adequately,[6-8] and the concentration dependence of ξ so obtained obeys a power law, $\xi \propto \phi^a$. Moreover, the exponents found agree reasonably well with scaling predictions:[9]

$$\xi \propto \phi^{-0.75} \qquad \text{good solvent}$$
$$\xi \propto \phi^{-1.0} \qquad \Theta \text{ solvent} \qquad (2)$$

It is not so difficult then to assume what seems obvious, namely $\xi = \xi_{ev}$. However, the range covered by the power law data is found to extend well into a moderately concentrated regime, where the length obtained is considerably smaller than the crossover length scale for the excluded volume $R_g^\ddagger$ and sometimes even smaller than the Kuhn length l_K of the species.

Therein lies the difficulty, as forcefully pointed out by several of those actually making the measurements, notably Brown and Nicolai[7] and more recently Tao et al.[8] The correlation length for a model polyethylene (M = 53 200), shown as a function of concentration for a good solvent hexadecane[8] in Figure 1, illustrates the problem. A power law with about the right exponent describes the data over a very wide range of concentration:

$$\xi(\phi)\ (\text{nm}) = 0.329\phi^{-0.76} \qquad 0.040 \le \phi \le 0.685 \qquad (3)$$

There is another possible interpretation of the scattering data that is unrelated to excluded-volume screening. It is a natural outgrowth of the de Gennes equation,[9,10] derived for Flory–Huggins mixtures with the random phase approximation:

$$\frac{C}{I_r(q)} = \frac{1}{\phi_1 V_1 P_1(q)} + \frac{1}{\phi_2 V_2 P_2(q)} - 2\frac{\chi(T)}{V_0} \qquad (4)$$

where I_r is the reduced coherent scattering intensity, C is the contrast factor, V_i, ϕ_i, and P_i are component molar volumes, volume fractions, and form factors, χ is the Flory interaction parameter, and V_0 is its arbitrary reference volume.

As it must, eq 4 shares the general limitations of the Flory–Huggins model. The assumption of spatial uniformity makes it inappropriate for scattering by dilute polymer solutions. It may also be inapplicable to scattering by semidilute solutions for properties such as screening length that reflect sub-R_g differences in local chain environment. Until now, eq 4 has been used primarily for the determination of chain dimensions and interaction strength in polymer blends.[11] From its success in even that complex environment, one might at least entertain the hope it would have some use for polymer solutions beyond ϕ^* in Θ solutions and beyond $\phi^\ddagger$ in good solvents.

In polymer solution terminology—component 1 is the solvent, $V_0 \equiv V_1$, $\phi_2 = \phi$, $P_1(q) = 1$ in the range of interest—eq 4 becomes

$$\frac{V_1 C}{I_r(q)} = \frac{1}{1-\phi} + \frac{V_1}{\phi V_2 P(q)} - 2\chi(T) \qquad (5)$$

in which $V_2/V_1 \gtrsim 10^3$ is approximately the degree of polymerization of the polymer, and $P(q)$ is the polymer form factor. At $q = 0$ the second term on the right, the polymeric contribution, is of order 10^{-3} or less. Hence, unless the solution is dilute, $\phi \lesssim 10^{-3}$, the polymer contribution is insignificant relative to the other two terms.

The situation changes for scattering in the intermediate q range. For random coils, $P(q) = 2/(qR_g)^2$ applies at intermediate q,[11] leading to

$$\frac{V_s C}{I_r(q)} = \frac{1}{1-\phi} - 2\chi(T) + \frac{1}{2\phi}\left(\frac{M_s \bar{v}_s}{\bar{v}_p}\right)\left(\frac{R_g^{\,2}}{M}\right)_p q^2 \qquad (6)$$

where the subscripts s and p now refer to solvent and polymer, and $\bar{v}_s$ and $\bar{v}_s$ are specific volumes. All quantities in eq 6 are known or can be determined by separate experiments, so the q-dependent scattering intensity can be predicted and compared with experiment.

Four sets of scattering data are used for the comparisons: the good solvent polyethylene–hexadecane (PE-C16) system[8] and three polystyrene systems, cyclohexane at the Θ condition[7] (PS–CHN) and two good solvents,[6] tetrahydrofuran (PS–THF) and methylene chloride (PS–MEC). Polymer properties such as R_g^2/M and melt density $\rho_p \sim 1/\bar{v}_p$ were taken from Fetters et al.;[12] the solvent properties are handbook values.[13] Obtaining interaction parameters for the systems was a problem. Values for polyethylene in various n-alkanes[14] were interpolated to obtain $\chi = 0.22$ for PE-C16. Nothing was found for the two polystyrene good solvent systems, PS-MEC and PS-THF, so the typical good solvent value,[14] $\chi = 0.4$, was used for both.

Considerable interaction parameter data are available for the Θ system PS–CHN.[15] Unlike good solvent systems, for which χ is relatively insensitive to polymer concentration, Θ systems—PS–CHN as well as polyisobutylene–benzene[16] and poly(dimethylsiloxane)–butanone[17]—exhibit significant concentration dependence. Θ systems are thus not Flory–Huggins mixtures, but perhaps the errors from that are not too large. For PS–CHN, the interaction parameter data for the range $0 < \phi \lesssim 0.8$ are well described by a quadratic expression:

$$\chi = a_0 + a_1\phi + a_2\phi^2 \qquad (7)$$

The generalization of eq 6 for an interaction parameter

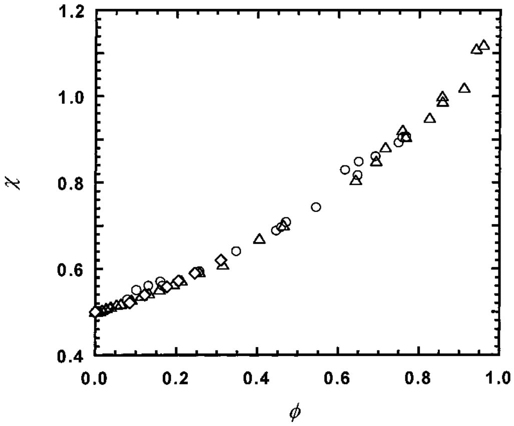

Figure 2. Interaction parameter as a function of concentration at the Θ condition for various polymer−solvent systems. The symbols denote data for polystyrene−cyclohexane at 34 °C (○), polyisobutylene in benzene at 24.5 °C (△), and poly(dimethylsiloxane) in 2-butanone at 25 °C (◇).

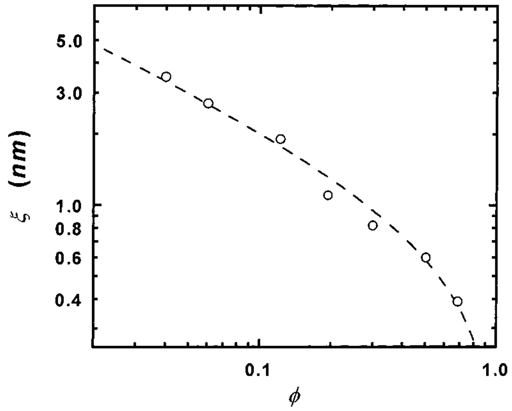

Figure 3. Comparison of correlation length for polyethylene in hexadecane with the result from eq 6 and $\chi = 0.22$. The dashed line indicates the calculation.

that depends on concentration is outlined in the Appendix. For the dependence given by eq 7, the scattering equation becomes

$$\frac{V_s C}{I_r(q)} = \frac{1}{1-\phi} - (2a_0 + 3a_1\phi + 4a_2\phi^2) + \frac{1}{2\phi}\left(\frac{M_s\bar{v}_s}{\bar{v}_p}\right)\left(\frac{R_g^{\,2}}{M}\right)_p q^2 \quad (8)$$

Surprisingly, as shown in Figure 2, the $\chi(\phi)$ data for all three Θ systems,[15−17] to the eye at least, fall along a single curve. The systems individually require slightly different sets of coefficients. Scattering curves were calculated with eq 8 for two sets, least-squares values with $a_0 = {}^1/_2$ fixed, one based on the PS−CHN data alone—$a_1 = 0.320$, $a_2 = 0.283$—and the other based on all three sets of $\chi(\phi)$—$a_1 = 0.267$, $a_2 = 0.365$.

Results and Discussion

To make comparisons as directly as possible, the calculated scattering curves for the four systems were worked up in the same manner as the experimental data. Thus, eqs 6 and 8 already have the Ornstein−Zernike form, $1/I(q) = A + Bq^2$, so $\xi = (B/A)^{1/2}$ is the calculated size. Figure 3 compares observed and calculated sizes for PE-C16. The dashed line is the calculated result, and the agreement is remarkably good. Figure 4a,b shows the results for the other two good solvent systems. The calculated sizes are smaller by 15−20% for PS−MEC and by 20−30% for PS−THF.

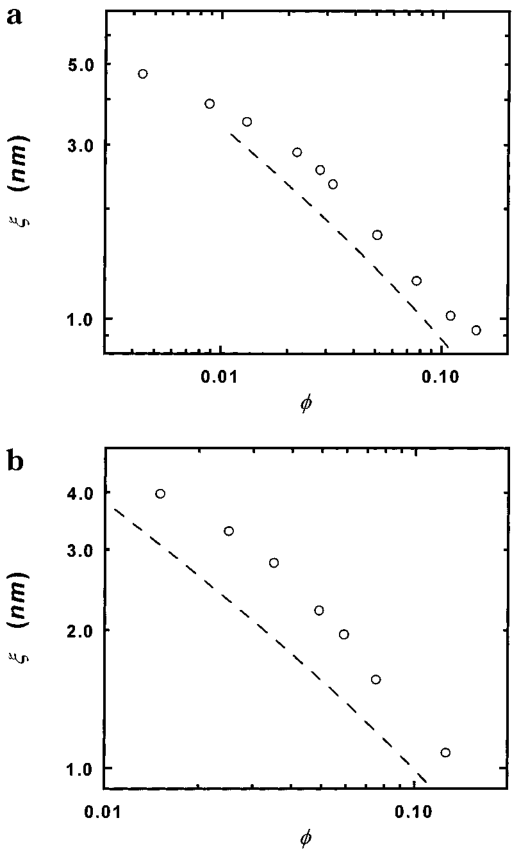

Figure 4. Comparison of correlation length for polystyrene in good solvents with the eq 6 calculation. (a) Data for methylene chloride solutions and the calculation for $\chi = 0.4$. (b) Data for tetrahydrofuran solutions and the calculation for $\chi = 0.4$.

The Θ system comparison in Figure 5a,b shows rather different results, depending on which set of coefficients is used. With coefficients based on PS−CHN interaction data, Figure 5a, the calculated curve passes through the scattering data region, but its shape is clearly different from the trend of the data. With coefficients based on all three data sets, Figure 5b, the scattering data and calculated curve agree fairly well in both shape and magnitude.

The comparisons in Figure 5 illustrate the sensitivity of Θ condition predictions to seemingly minor differences in χ vs ϕ behavior. Indeed, the choice to force $a_0 = {}^1/_2$ on the fits was made to avoid negative scattering intensities, meaning thermodynamic instability of the single-phase state, at low concentrations. An examination of eq 8 for $a_0 = {}^1/_2$ makes clear how it happens that the slope and curvature of χ vs ϕ, subject to considerable uncertainty even for good data, assume major importance in predictions of scattering behavior near the Θ condition. One would in fact expect similar sensitivity, especially for high molecular weight samples, when conducting SANS experiments in the Θ region.

In contrast to Θ systems, the calculated curves for good solvent systems are not strongly sensitive to χ vs ϕ details. The agreement between experiment and calculation can in fact be much improved by allowing some choice of χ within the observed range for good solvent systems. Thus, replacing $\chi = 0.40$ with $\chi = 0.46$ for PS−THF and with $\chi = 0.42$ for PS−MEC greatly

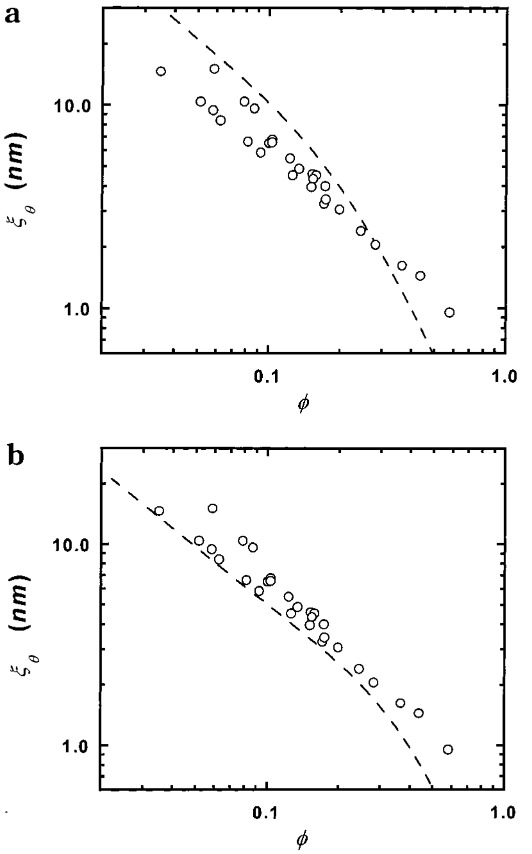

Figure 5. Comparison of correlation length for polystyrene in cyclohexane at Θ with the eq 8 calculation for two χ vs ϕ correlations. (a) The result with the polystyrene–cyclohexane correlation. (b) The result with the composite Θ-condition coefficients.

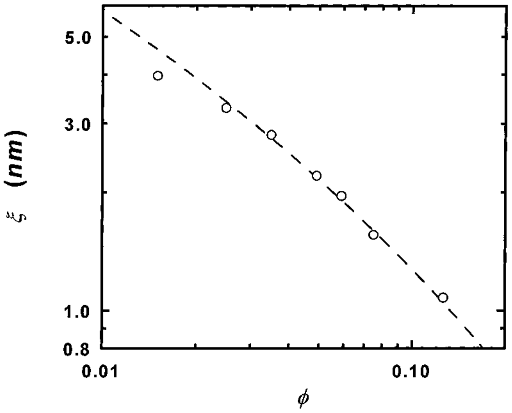

Figure 6. Comparison of correlation length for polystyrene–tetrahydrofuran solutions with χ arbitrarily adjusted from 0.40 (shown in Figure 4b) to 0.46.

improves the fits to the SANS data. Figure 6 shows the result of allowing that adjustment—near agreement in both shape and magnitude for the PS–THF example.

Concluding Remarks

It would appear from these various comparisons that eq 8 provides a satisfactory nonscreening interpretation of the correlation lengths that have been obtained from SANS data for polymer solutions. This does not of course conflict with the idea of excluded-volume screening and some corresponding length scale. Excluded-volume screening must certainly progress smoothly over some range of concentrations, R_g moving correspondingly from $R_g(0)$ to $(R_g)_\theta$. It is merely suggested that the change takes place over a rather narrow range beyond ϕ^* and that chain dimensions are essentially unperturbed over much of the concentration range. It is also conceivable that the scattering signature for partially screened volume exclusion is not very strong. In any case, since unperturbed chain dimensions form the basis of eq 8, there would seem to be no reason for believing that any significant change in R_g occurs throughout the upper range of concentrations covered by the SANS studies. The results are consistent with the estimate $\phi^\ddagger \sim 0.1$ for the crossover to melt chain dimensions and certainly so with the Westermann et al. observation that $R_g(\phi) \sim R_g(1)$ for at least the range $0.25 \leq \phi \leq 1$.

The interpretation and analysis of scattering behavior presented here indicate that the Ornstein–Zernike slope over intercept method is not the best way to analyze the data. From eq 6 or 8 with scattering intensity expressed in absolute units, the slope alone, $\mathrm{d}I_r^{-1}/\mathrm{d}q^2$, contains the size information and the intercept the thermodynamics. Aside from known or easily measured parameters, the size information is R_g^2/M, a property of the polymer species that should be independent of molecular weight and concentration above $\phi^\ddagger$. The small sizes obtained with the Ornstein–Zernike formula and interpreted as screening lengths are an artificial construct, unrelated to any physical length in the solution.

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Appendix

The values of χ were determined by fitting data on the chemical potential of solvent, $\mu_s - \mu_s^o$, obtained from osmometry or vapor sorption measurements,[15–17] to the Flory–Huggins expression:[14]

$$\chi(\phi,T) \equiv \frac{(\mu_s - \mu_s^o)/RT - \ln(1-\phi) - (1 - V_s/V_p)\phi}{\phi^2} \tag{9}$$

The scattering equation requires the derivative of the chemical potential:[11]

$$\frac{V_s C}{I_r(0)} = -\frac{1}{\phi RT}\frac{\partial \mu_s}{\partial \phi} \tag{10}$$

From the derivative calculated with eq 9 and the de Gennes generalization to finite q, the scattering equation then becomes

$$\frac{V_s C}{I_r(q)} = \frac{1}{1-\phi} + \frac{V_s}{\phi V_p P(q)} - \frac{1}{\phi}\frac{\partial \phi^2 \chi}{\partial \phi} \tag{11}$$

In the intermediate q region, with eq 7 and the various substitutions, the result is eq 8 of the text.

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