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Observations on Concentrated Polymer Solutions near the Θ Condition Using Small-Angle Neutron Scattering

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ABSTRACT: Small-angle neutron-scattering measurements are presented here for concentrated solutions of polystyrene–cyclohexane-*d* at and below the Θ temperature, 38 °C. The osmotic modulus, $\varphi(\partial\Pi/\partial\varphi)$, evaluated from the intensity, is found to vary faster than φ^3, where $\varphi = c/\rho$ is the polymer volume fraction, c being the concentration and ρ the density of the pure polymer. The polymer–polymer correlation length, ξ, however, which in the semidilute region conforms to the simple scaling relation, viz., $\varphi(\partial\Pi/\partial\varphi) \propto kT/\xi^3$, varies only as φ^{-1}. The observations are consistent with the Muthukumar–Edwards description of solutions, for which at the Θ temperature $\varphi(\partial\Pi/\partial\varphi) \propto \varphi^3/(1-\varphi) + z\varphi^3$, z being a function of the third-order interaction parameter, w. The value $z = -0.8_3 \pm 0.1_0$ deduced from the dependence of scattering intensity upon polymer concentration yields $w = 0.03_0 \pm 0.01_8$. In the single-phase region below 38 °C, the scattering intensity and correlation length both increase, also in agreement with the Muthukumar–Edwards theory.

Introduction

The neutron-scattering properties of semidilute solutions of polystyrene in cyclohexane at and above the Θ temperature were investigated some time ago by Cotton et al.[1] Their results provided support for the scaling analysis of Daoud and Jannink,[2] according to which semidilute polymer solutions can be described by a characteristic polymer–polymer correlation length ξ. In the neighborhood of the Θ temperature, ξ varies inversely with polymer volume fraction φ, i.e.

$$\xi = \xi_0\varphi^{-1} \qquad (1)$$

On a macroscopic scale, solution thermodynamics are defined by the osmotic pressure Π, which, in simple scaling, is connected to the correlation length by an ideal gas law of the form[3]

$$\Pi = AkT/\xi^3 \qquad (2)$$

A is a factor of the order of unity, k is the Boltzmann constant, T is the absolute temperature, and ξ^3 represents the volume of the elementary concentration fluctuations. The intensity of the signal at small scattering vector Q is

$$I(Q \rightarrow 0) = BkTf\varphi^2/K \qquad (3)$$

where B is a geometrical constant, f is the contrast factor between solvent and polymer, and $K \equiv \varphi(\partial\Pi/\partial\varphi)$ is the osmotic modulus of the solution. It follows from eqs 1–3 that the intensity should be proportional to

$$I(Q \rightarrow 0) \propto \varphi^{-1} \qquad (4)$$

Because simple scaling theory idealizes the polymer into an infinitely thin chain possessing length but no volume, the scheme introduced by Daoud and Jannink[2] has no intrinsic upper concentration bound for the semidilute Θ condition, apart from the material constraint that the polymer volume fraction φ be restricted to

$$\varphi \le 1 \qquad (5)$$

The original Flory–Huggins lattice model[3] is used as a starting point in more recent scaling theories[4,5] to incorporate the polymer volume into their formalism. In particular, Muthukumar[5] has derived formulas that allow the explicit calculation of the osmotic modulus K.

It is known from experimental[6-8] as well as theoretical[2,4,5,9] investigations that for semidilute polymer solutions at the Θ temperature the osmotic pressure varies as φ^3, in agreement with eqs 1 and 2.

The purpose of this paper is to chart the Θ solvent behavior of a polymer solution in a range of concentration higher than that of the semidilute regime (defined as $\varphi \ll 1$) and to relate it to the scheme of Muthukumar. Neutron-scattering measurements are performed for solutions of polystyrene in cyclohexane at and below the Θ temperature, for polymer volume fractions φ extending up to 0.7. The results of these measurements are compared with data from osmotic pressure observations found in the literature.

Theoretical Background

We briefly recall the Edwards–Muthukumar scheme,[4,5] the thrust of which was to calculate scaling corrections to the Flory–Huggins[3] lattice theory of solutions. The latter theory contains two principal thermodynamic parameters, χ and (optionally), w, which describe the second- and third-order polymer–polymer interactions, respectively. These quantities determine the expansion factor, α, and ξ/l, the polymer–polymer correlation length relative to an elementary step length, l. l is proportional to the bond length of the polymer backbone.[5] By a variational procedure, an expression is obtained in terms of these parameters for the free energy of mixing of the polymer solution. Due to correlations, this is lower than that for the standard Flory–Huggins expression. The algebraic

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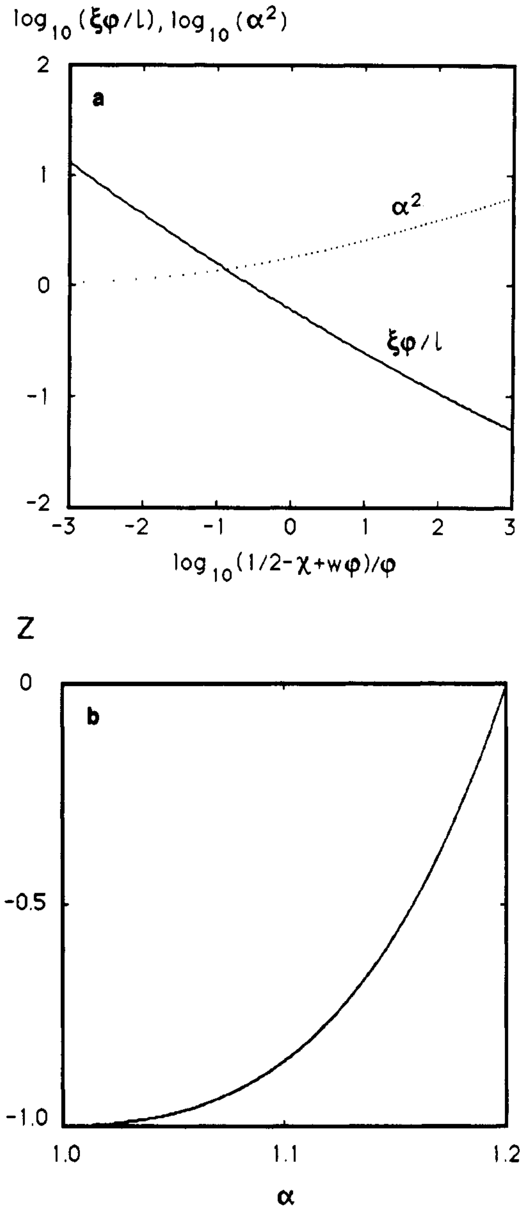

Figure 1. (a) Calculated values of reduced correlation length, $\xi\varphi/l$, (full line) and mean-square end-to-end coil expansion factor, α^2 (dotted line), in polymer solutions, as a function of the interaction strength, $(1/2 - \chi + w\varphi)/\varphi$ (from ref 5). (b) Calculated values of the parameter z as a function of the expansion factor α (from eqs 6, 10, and 11) in the Muthukumar theory[5] for the Θ temperature ($\chi = {}^1/_2$).

results of ref 5 lead to the relation

$$\frac{0.3376\alpha^6(\alpha^2-1)^2}{(1+0.2548(\alpha^2-1))} = \left(\frac{1}{2} - \chi + w\varphi\right)/\varphi \tag{6}$$

where it is understood that the interaction parameters χ and w are independent of concentration. Concomitantly, the correlation length is given by

$$\frac{\xi}{l}\varphi = \frac{1+0.2548(\alpha^2-1)}{1.4231\alpha^2(\alpha^2-1)} \tag{7}$$

Figure 1a shows the values of α^2 and $\xi\varphi/l$ that result from these two relations, as a function of the interaction strength $(1/2 - \chi + w\varphi)/\varphi$.

Here, we assume that the Θ condition in the concentrated state is identifiable with that for dilute solutions; namely, $1 - 2\chi = 0$. In the vicinity of this condition, it follows from eq 6 that α becomes independent of φ. The free energy of mixing (ref 5, eq 3.17) of a solution of polymer chains having degree of polymerization n is

$$\frac{\Delta G}{kT} = \frac{\varphi}{n}\ln\varphi + (1-\varphi)\ln(1-\varphi) + \chi\varphi(1-\varphi) + \left(w - \frac{1}{6}\right)\varphi^3 + (24\pi\xi^3)^{-1} - \frac{9}{16\pi}\,\frac{\left(\frac{1}{2} - \chi + w\varphi\right)\varphi}{\alpha^2\xi} \tag{8}$$

On differentiation, this yields for the osmotic pressure, Π, close to the Θ temperature

$$\Pi v_1/NkT = \varphi\rho/M - [\ln(1-\varphi) + \varphi + \chi\varphi^2] + z\varphi^3/3 \tag{9}$$

where v_1 is the molar volume of the solvent, N is Avogadro's number, ρ is the density of the pure polymer, and M is its molecular weight. When $\chi = {}^1/_2$ and $M = \infty$, eq 9 yields

$$K = \varphi\frac{\partial\Pi}{\partial\varphi} = \frac{NkT}{v_1}\varphi^3\left\{\frac{1}{1-\varphi} + z\right\} \tag{10}$$

in which z is given by

$$z = 6w - 1 + 6y \tag{11}$$

and where y is a function only of α. The value of z is governed by the monomer–monomer interaction w, and the factor $1 - \varphi$ defines the polymer volume fraction inaccessible to the solvent. From the numerical parameters adopted in eqs 3.9, 3.14, and 3.17 of ref 5, one obtains

$$y = 0.1147\left(\frac{\alpha^2(\alpha^2-1)}{1+0.2548(\alpha^2-1)}\right)^3 \times \left(\frac{1}{3} - \frac{3}{4}\{1 + 0.2548(\alpha^2-1)\}\right) \tag{12}$$

The principal difference between the Muthukumar–Edwards[5] and the classical Flory[3] expression for the free energy is that in the latter the correlation term y is absent. As may be seen from eqs 6 and 7, for χ close to ${}^1/_2$, ξ is proportional to φ^{-1}. K is proportional to ξ^{-3} only for small values of φ.

From inspection of eqs 6, 11, and 12 it can been seen that, in the absence of third-order interactions ($w = 0$, $\alpha = 1$), $z = -1$. At this condition, eq 7 states that $\xi\varphi/l$ diverges. In Figure 1b the dependence of z upon the parameter α is displayed, as calculated from eqs 6 and 12.

Experimental Conditions

The solutions were prepared from protonated polystyrene of molecular weight 2.0 × 10⁶ (Lot 14b, Pressure Chemical, $M_w/M_n < 1.20$) and perdeuterated cyclohexane (Janssen Chimica) without further purification. The use of a high molecular weight sample was motivated by the requirement to work in the asymptotic regime.

The components in their different proportions were placed in airtight bottles, weighed, and allowed to come to equilibrium over several weeks in an oven at 40 °C. The homogeneous solutions were transferred to the scattering cells, which consisted of two quartz windows separated by an airtight PTFE spacer of thickness 2.0 mm. The samples were then weighed and held at their lowest working temperature (18, 28, or 38 °C) for 2 days until the start of the scattering observations; 38 °C is the Θ temperature for the polystyrene–deuterated cyclohexane system.[1] Several hours were allowed to elapse between the time a temperature increase was applied to a sample and the scattering measurement.

No phase separation was observed to occur in any of the samples. This observation is in agreement with the temperature–concentration diagram of polystyrene–cyclohexane solutions of ref 1, according to which all the samples investigated here, even those at the lowest temperature, lie within the single-phase region.

At the end of the measurements, the samples were again weighed to check absence of solvent loss. They were then opened, dried in a vacuum oven, and weighed again. The concentration

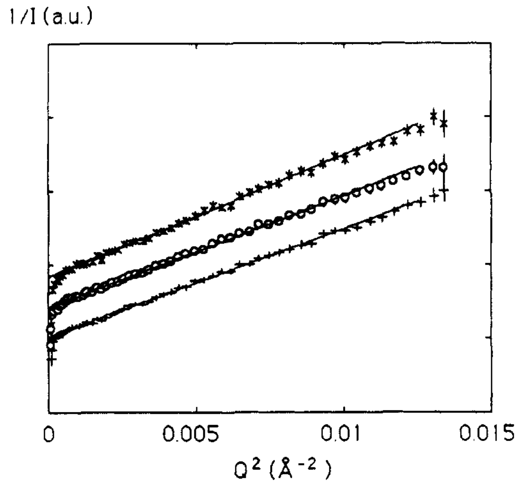

Figure 2. Zimm representation of the corrected scattering data from the solution of concentration $c = 0.57$ g cm^{-3} at three different temperatures: (*) 38 °C, (○) 28 °C, (+) 18 °C. Continuous lines are least-squares fits of Lorentzian curves to the data in the Guinier range.

was calculated by assuming volume additivity for the solvent and polymer, taking for the density of deuterated cyclohexane our measured value for protonated cyclohexane at 38 °C, namely, 0.766 g/cm^3, corrected for the ratio of molecular weights, 96/84. The volume fractions φ were obtained from the relation $\varphi = c/\rho$, in which c is the concentration in grams per cubic centimeter and ρ, the density of the pure polymer, is taken to be 1.05 g/cm^3.

The scattering measurements were made on the D17 instrument at the Institut Laue Langevin, using an incident neutron wavelength of 11 Å and a sample–detector distance of 2.85 m. To extend the accessible range of transfer wave vectors q, the detector was offset by 5 degrees from the incident beam. The q range explored was 0.009 Å$^{-1} \leq q \leq$ 0.12 Å^{-1}, and counting times of 1 h were used. After radial averaging, standard corrections for incoherent background, detector response, and cell window scattering were applied.

Results and Discussion

Figure 2 displays three representative scattering spectra, in which the data for a solution with $c = 0.57$ g/cm^3 at the three temperatures 18, 28, and 38 °C are shown in a Zimm plot. In all cases a straight line provides a plausible fit through the data points, except at the smallest q values. The excess scattering in the low q region, present in all the samples investigated, is typical of polystyrene solutions at sufficiently high concentrations and may be caused by associations among the macromolecules.[10,11] Such nonuniformities, also revealed by dynamic light-scattering measurements on similar samples as very slowly moving associations,[12] are expected to have little or no effect on the thermodynamics of the solution.

In all cases, least-squares fits were performed in the Guinier range $Q\xi \leq 1$. For the least concentrated sample, however, because of the perturbation from excess forward scattering, the fitting range $0.7 \leq Q\xi \leq 1.8$ was adopted. The correlation lengths and normalized intensities resulting from all the fits are listed in Table I.

In Figure 3 the correlation lengths are plotted as a function of polymer concentration in a double-logarithmic representation. In this same figure the data of ref 1, obtained from solutions of polystyrene of molecular weight 172 000 Da at the same nominal temperature (open circles), are also included. The present data tend to lie slightly above those of ref 1 (straight line), except for the point from our most concentrated sample, which is subject to the largest error. The smallest value of ξ measured, 5.5 Å, is greater than the lower bound for the elementary step length (bond length) implied in the theory[5] but is well below the value of the Kuhn step length measured in dilute solution (ca. 16 Å).[13]

Table I
Lorentzian Fitting Parameters to SANS Spectra

sample	concn, g/cm^3	temp, °C	intensity,[a] cm^{-1}	ξ, Å
1	0.153	38	19.8	43.5
2	0.365	38	4.4	16.3
3	0.43	38	3.6	14.4
4	0.57	38	1.6	9.6
5	0.71	38	0.74	5.5
3	0.43	28	5.1	17.2
4	0.57	28	2.0	10.4
4	0.57	18	2.7	12.0

[a] Normalized with respect to a 1-mm-thick H_2O sample at 25 °C with an incident wavelength of 11 Å.[15]

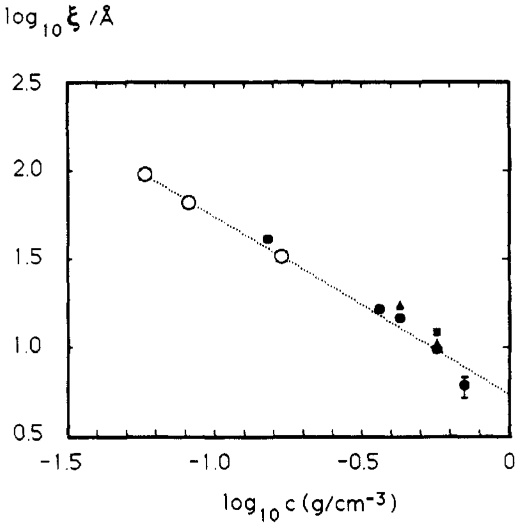

Figure 3. Concentration dependence of the correlation length in polystyrene–cyclohexane, in the double-logarithmic scale: open circles, ref 1; filled circles, this work, T = 38 °C; triangles, 28 °C; square, 18 °C. The straight line shown has a slope −1.

The increase of ξ with decreasing temperature, visible in Table I, is in qualitative agreement with the relationship between $\xi\varphi/l$ and $(1/2 - \chi + w\varphi)$ displayed in Figure 1: a reduction in the temperature causes an increase in χ, and hence also in $\xi\varphi/l$.

The interaction term z of eqs 10 and 11 can be evaluated from the experimental data. Equations 3 and 10 allow the zero-angle scattering signal intensity, $I(0)$, to be written in the form

$$\frac{1}{I(0)\varphi} = \frac{N}{Bfv_1}\left(\frac{1}{1-\varphi} + z\right) \tag{13}$$

If the osmotic modulus $K = \varphi\partial\Pi/\partial\varphi$ were proportional to φ^3, then the quantity $1/I(0)\varphi \propto K/\varphi^3$ would be independent of φ. Figure 4 shows the extrapolated signal at 38 °C, corrected for sample transmission, plotted in the representation $1/I(0)\varphi$ vs $1/(1-\varphi)$. The observed dependence of $1/I(0)\varphi$ indicates that K varies more strongly than φ^3, in agreement with the Muthukumar theory. The straight line through the points of Figure 4 yields the intercept

$$z = -0.8_3 \pm 0.1_0 \tag{14}$$

Insertion of this value for z into eqs 10 and 11 gives

$$\alpha = 1.11 \pm 0.03 \tag{15a}$$

and

$$w = 0.03_0 \pm 0.01_8 \tag{15b}$$

The numerical value of $\xi\varphi/l$ corresponding to eq 15 can

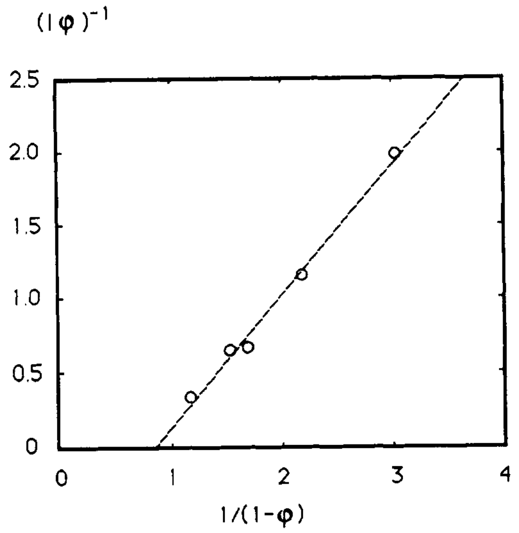

Figure 4. Concentration dependence of $1/I(0)\varphi$ vs $1/(1-\varphi)$ in polystyrene–cyclohexane. The normalized intercept of the least-squares straight line at the origin is $z = -0.83 \pm 0.10$.

be calculated from eq 7 to be

$$\xi\varphi/l = 2.7 + 1.5 \text{ or } -0.5 \qquad (16)$$

The value found for α in eq 15a clearly indicates the importance of the three-body interaction in the concentrated Θ solution investigated here. In the absence of three-body interactions, the Muthukumar theory asymptotically reduces to the mean-field Flory–Huggins theory for a Θ system, i.e., $\alpha = 1$, while $\xi\varphi/l$ diverges. In agreement with this picture, the value of y found here ($y = -0.001$) is much smaller than z and w.

The straight line of Figure 3 corresponds to $\xi\varphi = 5.3$ Å, which, in conjunction with eq 16, finally yields an elementary step length of

$$l = 1.9 \pm 0.5 \text{ Å} \qquad (17)$$

This estimate is consistent with the carbon–carbon bond length in polystyrene (1.54 Å).

The above neutron-scattering results may be compared with existing osmotic pressure observations. Few data are available in the literature reporting osmotic pressures in solutions up to sufficiently high concentrations for such comparisons to be meaningful. The osmotic pressure measurements of Vink,[6] performed in the range $0.014 \leq \varphi \leq 0.12$, seem to be the best data set published so far on polystyrene–cyclohexane solutions at 37 °C (i.e., slightly above the Θ temperature for PS in protonated cyclohexane). Equation 9 can be rewritten in the form

$$\Pi v_1/NkT + [\ln(1-\varphi) + \varphi] = \varphi\rho/M - \chi\varphi^2 + z\varphi^3/3 \qquad (18)$$

Application of a three-parameter linear regression fit to the data points of Vink[6] yields $M = 119\,000$ Da, $\chi = 0.497$, and $z = -0.97$. In view of the difference between the concentration ranges explored in the osmotic pressure measurements and the present neutron-scattering observations and also of the difference between the experimental techniques involved, the agreement between the respective values of z is reasonably satisfactory.

Conclusions

In this paper the predictions of a recent theory of polymer solutions due to Muthukumar and Edwards are compared with the results of neutron-scattering experiments performed on polystyrene–cyclohexane solutions at the Θ temperature in the concentrated regime.

The small-angle neutron-scattering measurements presented here indicate that the osmotic modulus varies significantly faster than φ^3. The polymer–polymer correlation length, ξ, however, varies only as φ^{-1}. This deviates from the ideal gas behavior of simple scaling, according to which $\varphi(\partial\Pi/\partial\varphi)\xi^3/kT$ is a constant. Both of these findings are in agreement with the theory of Muthukumar.

The third-order interaction term, w, plays an important role. For the present system, the value found for w is $0.03_0 \pm 0.01_8$. The Muthukumar analysis yields for the step length 1.9 ± 0.5 Å, which is comparable to the length of a polystyrene backbone bond.

At temperatures below 38 °C in the single-phase region, the increase observed both in scattering intensity and in correlation length is consistent with the Muthukumar theory.

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Registry No. Neutron, 12586-31-1; polystyrene, 9003-53-6; cyclohexane, 110-82-7.