Small-angle neutron scattering from polymer solutions:
4. The semi-concentrated region near the lower critical solution temperature

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Small-angle neutron scattering has been used to determine the radius of gyration of polystyrene in a concentrated cyclohexane solution (0.477 g ml^{-1}) over the temperature range 69° to 220°C. The results have been interpreted by combining the corresponding states theory of polymer solution thermodynamics with recent theories of polymer dimensions. Although only qualitative agreement between theory and experimental results was obtained, the basic underlying principles of the theoretical description seem to be confirmed.

INTRODUCTION

Considerable experimental evidence now exists to support the general predictions of renormalization group theory of polymer solutions. In particular, evidence for regions of different behaviour near the upper critical solution temperature (*UCST*), the familiar Flory θ temperature, has been obtained not only from small-angle neutron scattering (SANS) experiments[1-4], but also from osmotic pressure[5] and observations of dynamic properties of polymer solutions[6]. The scaling law formulae describing this 'tricritical' behaviour of a polymer have also been derived without the use of renormalization group theory[7]. Furthermore, Edwards and Jeffers[8] have independently obtained the scaling law formulae for polymer dimensions in solution by applying limiting conditions to an extrapolation formula derived from mean field theory. In particular, for the case of strong screening and at high polymer concentration another behaviour region is predicted in addition to those postulated by the tricritical approach which we refer to as the semi-concentrated region. Parts 1 and 2[3,9] of this series presented evidence from SANS experiments for the existence of this semi-concentrated region near the *UCST*.

We have also shown that tricritical behaviour is evident near the lower critical solution temperature (*LCST*)[10]. Although exact agreement with scaling law formulae was not observed, definite crossovers in behaviour were clearly apparent near the *LCST*. In this paper we report the results of SANS experiments on a semi-concentrated solution of polystyrene in cyclohexane near the *LCST*.

EXPERIMENTAL

Materials

Cyclohexane and deuterocyclohexane were used without further purification. Hydrogenous polystyrene (PSH, $\bar{M}_w = 6.11 \times 10^4$; $M_w/M_n = 1.29$) and deuterated polystyrene (PSD, $\bar{M}_w = 7.57 \times 10^4$; $\bar{M}_w/\bar{M}_n = 1.54$) were prepared by anionic polymerization and characterized by gel permeation chromatography.

Measurement of mean square radius of gyration $\langle s^2 \rangle_w$

A solution of polystyrene in cyclohexane was prepared with a total polymer concentration of 0.477 g ml^{-1} at 25°C. Of the total weight of polymer present in solution, 0.02 g ml^{-1} was fully deuterated polystyrene, the remainder being made up of PSH. Aliquots of this solution were placed in 2 mm internal diameter silica tubing which were flame-sealed under vacuum after degassing the solution. A solution of PSH alone in cyclohexane at the same concentration as the test solution above, was also sealed into silica tubes. Although all solutions appeared to be homogeneous at room temperature, they were kept at ~40°C for some time preceding the actual measurements.

The possibility of degradation of the polymer was checked by repeating the experiment at the lowest temperature (69°C) after the complete cycle of measurements had been made. The same value of $\langle s^2 \rangle_w$ was obtained indicating that degradation was negligible.

Small-angle neutron scattering measurements on the test solution (that containing PSD) and the background solution (containing PSH alone) were made using the D11 diffractometer at the Institut Laue–Langevin, Grenoble, France[11]. Tubes containing the solution were maintained

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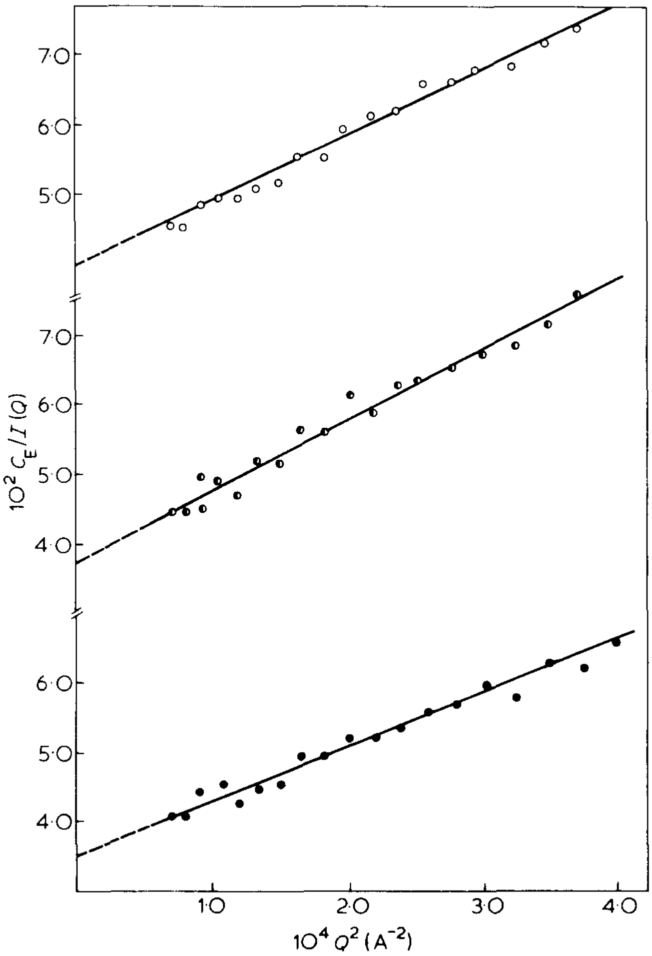

Figure 1 Zimm plots of scattered neutron intensity, $I(Q)$, as a function of Q for polystyrene (C = 0.477 g ml^{-1}) in cyclohexane. ●, 65°C; ◐, 138°C; ○, 201°C

at ± 0.2°C of the experimental temperature in a thermostatically-controlled holder. Experimental temperatures ($69 \leqslant T$ (°C)$\leqslant 220$) were measured by a thermocouple located near the experimental sample tubes. The range of scattering vector, $Q[=(4\pi/\lambda)\sin\theta/2]$ used was $0 < 10^2\ Q, \leqslant 2$ Å^{-1}.

The intensity of neutrons [$I(Q)$] scattered at a scattering vector Q due to the PSD chains was obtained by subtracting the scattering of the background solution from that of the test solution. The data was then interpreted using equation (1):

$$\frac{K^*C}{I(Q)} = \bar{M}_w^{-1}[1 + (\langle s^2\rangle_z/3)Q^2] + 2A_2C \qquad (1)$$

where $\bar{M}_w$ = weight-average molecular weight; C = polymer concentration; K^* = instrumental constant; A_2 = second virial coefficient; $\langle s^2\rangle_z$ = 'z'-average mean square radius of gyration.

Other experiments have shown that A_2 in equation (1) is zero for concentrated solutions[1] and consequently we have neglected this factor here.

RESULTS

Representative data plotted according to equation (1) are shown in *Figure 1*. From such plots, z-average mean square radii of gyration were calculated and subsequently corrected to weight-average values by the relationship:

$$\langle s^2\rangle_w = \langle s^2\rangle_z \left\{\frac{h+1}{h+2}\right\}$$

where

$$h = [(\bar{M}_w/\bar{M}_n) - 1]^{-1}$$

The dependence of $\langle s^2\rangle_w$ on temperature is shown in *Figure 2* which includes data between 10° and 65°C obtained from earlier experiments. A smooth curve has been drawn through the points as a guide to the eye.

DISCUSSION

Delmas and Patterson[12] have investigated the swelling behaviour of crosslinked polystyrene spheres in cyclohexane between 45° to 250°C. A maximum in the swelling ratio (= swollen volume/dry volume) of ~2.75 was noted at a temperature of 150°C. If we assume that the crosslinked polymer chains undergo affine deformation, then the cubic expansion factor (α^3) of the chains will also equal 2.75. Our data in *Figure 2* show a maximum at approximately 140°C and from the ratio of $\langle s^2\rangle_w$ at this temperature to the theta dimensions [$\langle s^2\rangle_\theta = 4.24 \times 10^3$ Å^2], a value of 2.6 for α^3 is obtained. The agreement between the two experiments is remarkably close in view of the different manners by which α^3 is calculated.

An exact expression for the mean square end-to-end distance $\langle r^2\rangle_w$ of a polymer chain in this semi-concentrated regime has been derived in terms of monomer density, ρ, and the excluded volume per segment, β. Two independent derivations have been published[8,13], both have the same general form differing only in the numerical factors. The general form of this expression given in equation (2) below:

$$\langle r^2\rangle_w = C_\infty n l^2 (1 + K\beta^{1/2}\rho^{-1/2}) \qquad (2)$$

where C_∞ is the characteristic ratio of the polymer and n is the number of bonds of length l in the chain. K is a factor composed of a numerical term and constants.

$$K = 4.(6)^{1/2}/\pi l^3$$

Edwards and Jeffers[8], or

$$K = 3.(3)^{1/2}/\pi l_0^3$$

Moore and Al-Naomi[13].

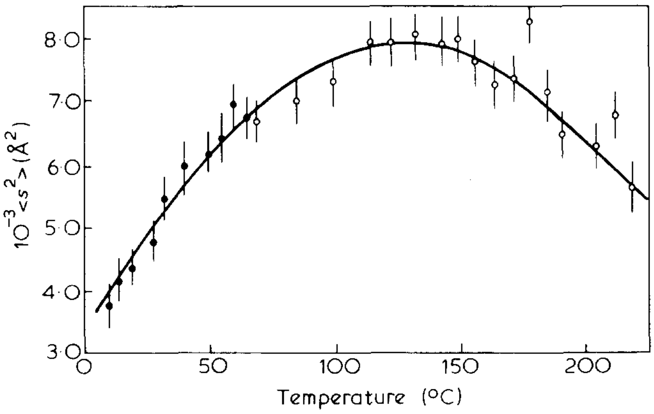

Figure 2 Variation of radius of gyration of polystyrene in cyclohexane with temperature. ●, Earlier results[3]; ○, present work

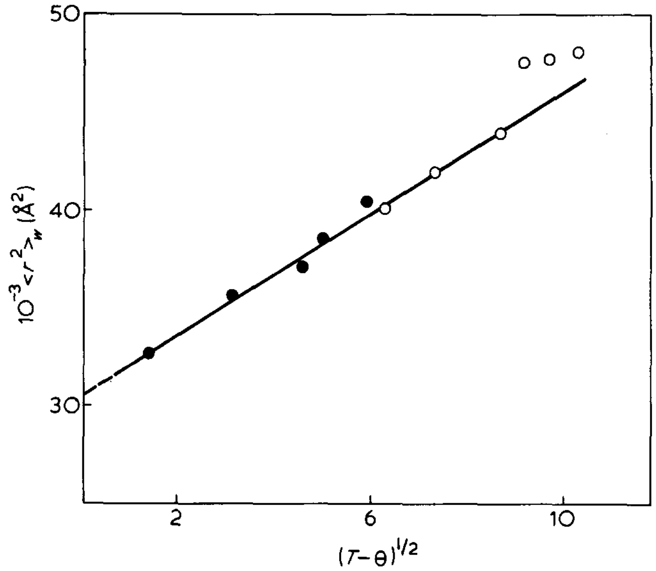

Figure 3 End-to-end dimensions of polystyrene in cyclohexane as a function of $-(T-\theta)^{1/2}$. Symbols as in *Figure 2*

Near the *UCST*, the excluded volume, β, has been represented by a $(T-\theta)$ temperature dependence[14], where $\theta = UCST$. Earlier data published in Part 1[3] has been shown to obey the temperature variation predicted by equation (2). This earlier data together with present data up to ~136°C are plotted as a function of $(T-\theta)^{1/2}$ in *Figure 2*. A straight line dependence on $(T-\theta)^{1/2}$ up to ~100°C is observed for $\langle r^2\rangle_w$ where $\langle r^2\rangle_w = 6\langle s^2\rangle_w$. Above this temperature the data falls well away from the best line drawn through the points.

At temperatures greater than 140°C the dimensions decrease with increasing temperature. Since $(T-\theta)$ increases linearly with *T*, this representation of the excluded volume can no longer be applied. Evidence from dilute solution experiments[11,15,16] supports the supposition that at the *LCST*the excluded volume is again zero, i.e. the polymer chain returns to its apperturbed dimensions. With this knowledge we can retain the form of equation (2) by writing $\beta^{1/2} \propto -(|T-\theta_L|^{1/2})$ where θ_L is the *LCST*. Using this expedient the linear form of equation (2) is retained and the excluded volume vanishes at the *LCST*. For temperatures in excess of 130°C, values of $\langle r^2\rangle_w$ have been plotted against $-(|T-\theta_L|^{1/2})$ in *Figure 3*, with $\theta_L = 213$°C, a value obtained from phase separation studies[17]. The points fit reasonably well on a straight line. From the intercept of the best fit line drawn a value for the characteristic ratio C_∞, may be obtained. This ratio is calculated to be 9.9 ± 0.7 (using $l = 1.54$ Å) and is in excellent agreement with the value of 10.0 obtained by conventional dilute solution studies in theta solvents[18].

For a more generalized discussion of the data, recent theories of polymer solution thermodynamics have to be invoked. The *LCST* of a polymer solution is a general phenomenon intimately associated with the volumetric properties of the solvent vis-a-vis those of the polymer. Primary characteristics of an *LCST*in polymer solutions are that both the enthalpy and entropy of dilution are negative. The negative volume change on mixing a polymer with a 'monomeric' liquid is responsible for these two observations, and, qualitatively, the solvent is pictured as being 'condensed' onto the polymer molecules.

Such phenomenological descriptions are quantified in the corresponding states theory of polymer solution thermodynamics, developed by Patterson and coworkers[19,20] and the equation of state theories produced by Flory and collaborators[21,22]. In their essentials both theories are identical. Each contain two parameters which describe the entropy and enthalpy of mixing a polymer with a solvent. These parameters can be written in terms of a reduced pressure, volume and temperature. Both theories have an empirical content in that agreement with experimental data has to be forced by arbitrary adjustment. Both theories give an equation for the temperature dependence of the polymer–solvent interaction parameter, χ_1, which is directly related to the excluded volume given by[23]:

$$\beta = \frac{\bar{v}_2^2 m^2 2}{V_1 N_A} \psi_1 (1-\theta/T)$$

where V_1 = solvent molar volume; m = monomer molecular weight; V_2 = partial specific volume of polymer. But

$$\psi_1(1-\theta/T) = (1/2-\chi_1)$$

$$\therefore \beta = \frac{\bar{v}_2^2 m^2 2}{V_1 N_A}(1/2-\chi_1) \tag{3}$$

thus the temperature dependence of β may be calculated from a knowledge of χ_1.

We have used the corresponding states expression ofr χ_1 [19] given by equation (4):

$$\chi_1 = -(U_1/RT)v^2 + (C_{p1}/2R)\tau^2 \tag{4}$$

In this equation, $-U_1$ is the energy of vaporization of the solvent and C_{p1} its configurational heat capacity, v^2 is related to the difference in cohesive energy and size between solvent molecules and polymer segments, whilst τ^2 characterizes the free volume change on mixing a polymer with a solvent. For the purpose of calculating χ_1, equation (4) may be written as[15,17,19]:

$$\chi_1 = \frac{c_1 v^2}{(1-\tilde{V}_1^{-1/3})} + \frac{c_1 v^2}{2\{\frac{4}{3}\tilde{V}_1^{-1/3}-1\}} \tag{5}$$

where $3c_1$ is the number of external degrees of freedom of a solvent molecule and may be calculated from the reduced pressure, volume and temperature of the solvent. The reduced solvent volume, $\tilde{V}_1$, at any temperature T is calculable from the solvent thermal expansion coefficient α_1:

$$\tilde{V}_1 = \left\{\frac{\alpha_1, T}{3(1+\alpha_1 T)} + 1\right\}^3 \tag{6}$$

To calculate $\tilde{V}_1$ as a function of temperature, an expression for α_1 of cyclohexane was used which was obtained from the work of Wood and Gray[24]. These values were used to calculate χ_1 from equation (5), the temperature dependence of which is plotted in *Figure 4*. This Figure also shows the separate contributions of the $(c_1 v^2)$ and $(c_1 \tau^2)$ terms, where values of 0.016 and 0.120 have been used for $c_1 v^2$ and $c_1 \tau^2$, respectively. These values have been calculated by Saeki *et al.* from their experimental phase separation data[17]. It has also been

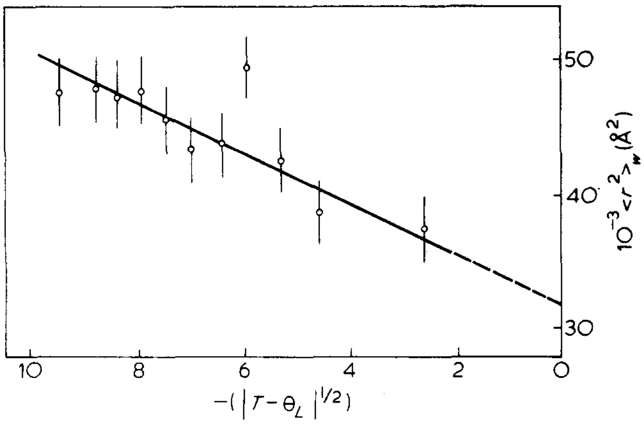

Figure 4 End-to-end dimensions of polystyrene in cyclohexane as a function of $-(|T-\theta_L|^{1/2})$

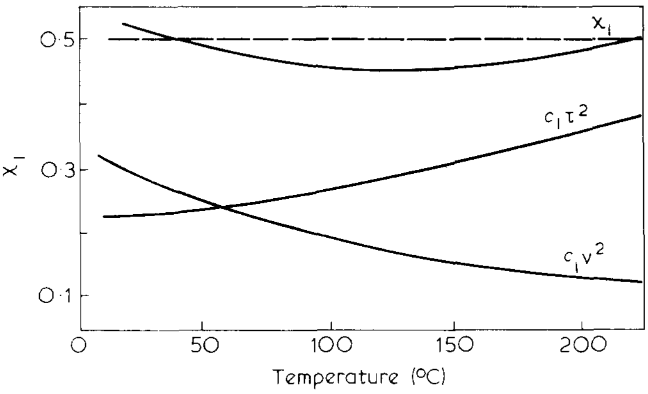

Figure 5 The temperature dependence of the χ_1 parameter for polystyrene in cyclohexane estimated from equation (5), and showing the separate contributions of the $c_1\nu^2$ and $c_1\tau^2$ terms

necessary to use an arbitrary shift of +76° along the temperature axis to obtain $\chi_1 = 0.5$ at the *UCST* and the *LCST*. With regard to this temperature shift, we note that a semi-empirical modification to corresponding states theory has been made by Cowie and McEwen[25]. This modification removes the necessity of making such arbitrary shifts of temperature and results in slightly different values of $c_1\nu^2$ and $c_1\tau^2$. However, the values of χ_1 calculated using these newer values are negligibly different from those calculated using the data of Saeki *et al.* and consequently do not influence the conclusions we have made (see below).

Values of χ_1 at various temperatures between 38° and 213°C have been used to calculate the excluded volume, β, given by equation (3). In their turn these values of β have been used in equation (2) to calculate $\langle r^2\rangle_w$ using $l = CN_A/m$. For all of these calculations, due notice has been taken of the temperature variation not only of χ_1, but also the polymer concentration, the solvent molar volume and the polymer partial specific volume. For this latter term, which we equate to (density)$^{-1}$, the expression of Höcker, Blake and Flory[26] has been used.

The calculation also requires values of the step length, l_0. We have obtained a value for this quantity by the following means. Under theta conditions:

$$\langle r^2\rangle_\theta = Ll_0$$

where l_0 is the step length and:

$$L = Nl_0$$

where N is the number of steps. But also

$$\langle r^2\rangle_\theta = C_\infty nl^2$$

and we know that the equivalent chain and the real chain must have the same end-to-end distance at full extension. Therefore:

$$nl = Nl_0$$

hence

$$l_0 = C_\infty l$$

Results of the calculations of $\langle r^2\rangle$ are shown in *Figure 5* as values of $\langle s^2\rangle$ ($\equiv \langle r^2\rangle/6$) together with the experimental values of $\langle s^2\rangle$. Qualitatively, both theoretical curves reproduce the observed behaviour in that a maximum in the radius of gyration as a function of temperature is produced. However, the absolute values are considerably smaller then the experimental $\langle s^2\rangle$ results especially at the maximum point.

We believe that the major source of this disagreement is the calculation of χ_1. No account has been taken of the concentration dependence of this parameter. Furthermore the data for cyclohexane used in calculation of $\tilde{V}_1$ was obtained in a temperature region far removed from the region 100° to 200°C.

Consequently, the linear extrapolation may not be valid here. Additionally, there have been three independent derivations of equation (2)[8,13,27], each of which has a different value for K. Notwithstanding this variation in K, all the theoretical formulae give values of $\langle s^2\rangle$ of the same order of magnitude as the theoretical lines in *Figure 5*.

CONCLUSIONS

By using a semi-empirically-modified relationship between excluded volume and temperature near the *LCST*, it is possible to retain the linear variation of chain dimensions postulated by the theoretical equations. From the best fit straight line through the data, the value for the characteristic ratio, C_∞, is in excellent agreement with

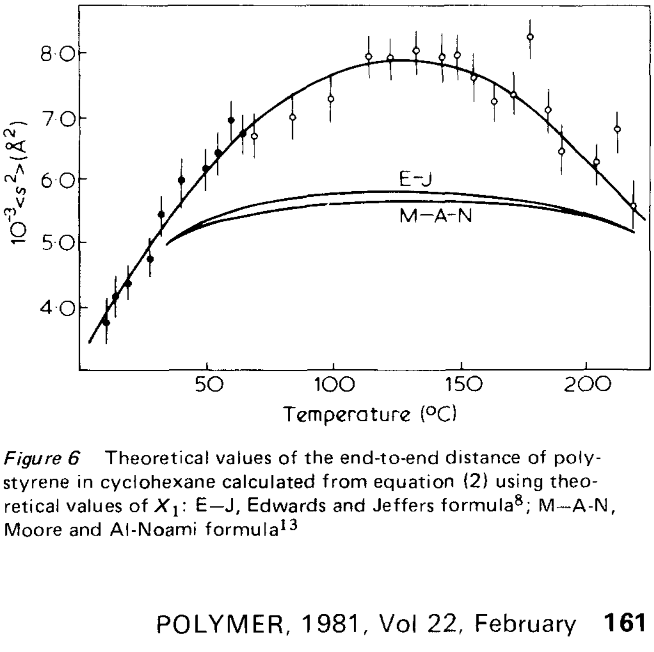

Figure 6 Theoretical values of the end-to-end distance of polystyrene in cyclohexane calculated from equation (2) using theoretical values of X_1: E—J, Edwards and Jeffers formula[8]; M—A-N, Moore and Al-Noami formula[13]

other data which is some confirmation of the general applicability of the mean field theory in this temperature range.

Notwithstanding the gross disagreement between absolute theoretical predictions and our experimental results, it is evident that the combination of corresponding states theory with formulae obtained from a mean-field-type theory is able qualitatively to reproduce the experimentally observed variation of chain dimensions with temperature. This is, in some measure, support for the postulate that a semi-concentrated region of behaviour exists near the lower critical solution temperature as well as the tricritical behaviour reported in Part 3.

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