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

Randal W. Richards*
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK
and Ann Maconnachie and Geoffrey Allen
Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2BY, UK
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Small-angle neutron scattering experiments have been made on solutions of polystyrene in cyclohexane. From these experiments the radius of gyration has been determined as a function of polymer concentration at a fixed temperature (60°C). Additionally, the screening length has been determined as a function of temperature for a fixed polymer concentration of 36% (w/v). The results support the notion of an additional region of solution behaviour, the semi-concentrated region, predicted by mean field-type theory.

INTRODUCTION

Great insight into the nature and properties of polymer solutions has been achieved in the last four or five years. This development can be traced to a paper by Edwards on the free energies of concentrated polymer solutions[1]. A self-consistent-field theory was used to derive expressions for the free energy. More recently the problem has been re-analysed using renormalization group theory[2] first developed by Wilson[3] for magnetic spin systems. Both approaches predicted that regimes of different behaviour should be observed depending on the concentration of the solution. Subsequently the earlier self-consistent-field theory was refined[4] and shown to produce equations which were similar (but not identical) to those obtained by renormalization group theory.

Examination of these theories has been made possible by the application of small-angle neutron scattering (SANS) to polymer solutions. Earlier experiments by ourselves (Part 1 of this series)[5] and, independently, by others, have confirmed the existence of these different regimes[6]. The results are in general agreement with the theoretical predictions relating chain dimensions to concentration and temperature in the neighbourhood of the upper critical solution temperature (Flory θ temperature) of the solution.

Our earlier experiments produced evidence for an additional region of behaviour not predicted by renormalization group theory but described by the Edwards mean-field formula. This region is at a higher concentration than the semi-dilute solutions and approaches the concentrated region. For this reason we call such solutions semi-concentrated.

In this paper, the physical basis of current theories of concentrated polymer solutions are presented and the implications for SANS experiments are outlined. Further evidence is presented to support the existence of the semi-concentrated region near the upper critical solution temperature. The additional supporting data concerns the dependence of radius of gyration on total polymer concentration, and the temperature dependence of the screening length in a semi-concentrated solution.

THEORY

Our intention here is not to re-derive or comment critically on any of the theories discussed. A physicochemical description of each of the two main theoretical approaches is presented and the resultant formulae discussed with a view to the experimental outcome.

The foundation of both approaches is the notion of screening first advanced by Edwards[1]. In a dilute solution where polymer chains are well separated from each other, intramolecular segmental interactions take place which are the source of the excluded volume[7]. As the concentration of polymer chains is increased intermolecular interaction now becomes evident. These intermolecular interactions screen distant segments of the same chain from each other and hence the influence of the excluded volume is weakened. The average distance along the chain between two such intermolecular interactions is the screening length (ξ) which may be defined as the distance beyond which there are no excluded volume interactions between any two segments separated from each other along the chain.

Hence for a given polymer the conformational behaviour in solution is determined by (i) the step length, (ii) the total length of the chain, (iii) the monomer density, ρ, i.e. the number of statistical units in the solution, which depends on the total number of polymer chains in the

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* To whom correspondence should be addressed.

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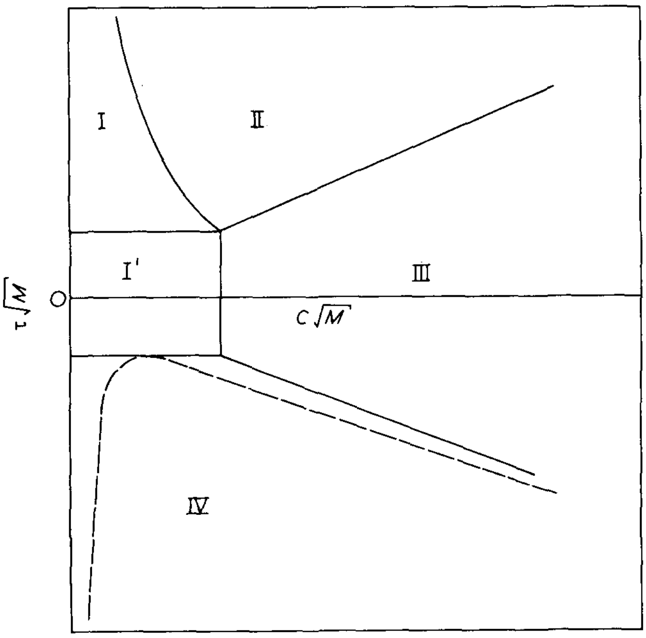

Figure 1 Phase diagram of polymer solution behaviour obtained by application of renormalization group theory

solution, (iv) the excluded volume (β) per statistical unit. Edwards[1] was then able to distinguish three regimes wherein the solution free energy behaviour differed. These three regimes were:

the dilute regime where chains are well-isolated from each other, i.e. $N\langle r^2\rangle^{3/2} < \beta$, where N = number of chains in solution and $\langle r^2\rangle$ is the mean square end-to-end distance;

the intermediate concentration (semi-dilute and semi-concentrated) regime, where polymer chains interpenetrate each other but the monomer density is not large, i.e. $N\langle r^2\rangle^{3/2} > \beta$;

finally there is the dense regime where every monomer unit is in contact with several others, i.e. $\rho\beta \simeq 1$ (where $\rho = Nn/v$ with N being number chains with n monomer units in volume v). The application of renormalization group theory and the associated scaling arguments to polymer solutions arose from an analogy between polymer solutions and magnetic critical point phenomena pointed out by de Gennes[8] and des Cloizeaux[9]. Full application of renormalization group theory could be made after de Gennes identified the θ point of polymer solutions as identical with the tricritical point of magnetic systems[10]. For application of this theory the polymer chain is viewed as a series of 'blobs' of diameter ξ ($\equiv$ screening length). Within the blobs excluded volume effects prevail but are absent over distances greater than ξ[11]. The blob diameter is dependent on the solution conditions, i.e. the four parameters (i) to (iv) outlined above. Using this model and renormalization group theory Daoud and Jannink[12] were able to construct a diagram in a temperature–concentration plane of the regimes of a solution in which different behaviour should be observed. Because of its similarity to conventional mixture phase diagrams, the resulting construction is called a 'phase' diagram of polymer solution behaviour. *Figure 1* shows the theoretical diagram with each of the behaviour regimes marked.

Phase diagram and the behaviour regimes

The phase diagram is in the plane of τ and concentration, C, where τ is $(T-\theta)/\theta$. Multiplication of these values by $\sqrt{M}$ (M = molecular weight) removes any dependence on molecular weight. Consequently $\tau M^{1/2} = 0$ corresponds to the theta point of the polymer solution.

Region I'. Here the polymer chain has unperturbed dimensions over a small range of temperature and concentration due to the molecular weight being finite.

Region I. Dilute good solvent regime: polymer molecules are widely separated and excluded volume effects prevail.

Region II. Intermediate concentration or semi-dilute region where molecules overlap to a certain extent. The concentration at which this overlap begins, C^*, may be defined as:

$$3M/4\pi N_A\langle s^2\rangle^{3/2} \leqslant C^* \leqslant M/N_A\langle s^2\rangle^{3/2}$$

where $\langle s^2\rangle$ = mean square radius of gyration.

Region III. Dense regime where each monomer segment is in contact with many others.

Region IV. The two phase region, below the theta point, where the polymer precipitates out of solution.

Daoud and Jannink[12] were able to obtain expressions for the screening length, ξ, and the mean square radius of gyration, $\langle s^2\rangle$, for a polymer chain in regions I' to III.

Subsequently, mean-field-theory has been reapplied to concentrated polymer solutions by Edwards and coworkers[4]. They were able to obtain more or less identical relationships to those obtained by scaling. More importantly, these relationships were obtained from a single formula which is able to extrapolate from infinitely dilute solution to bulk polymer. The various regions of behaviour are obtained by setting conditions for ρ and β. From this approach, a more acceptable picture of a polymer solution emerges, i.e. gradual changes from one region to another take place as temperature and/or concentration are changed.

Table 1 sets out the expressions for the mean square radius of gyration and the screening length obtained by scaling laws (*SL*) and mean-field (*MF*) theories for each of the regions in *Figure 1*. Referring to *Table 1*, it is clear that there is generally excellent agreement between the two approaches. It is in the intermediate concentration regime that differences are apparent, regions II and IIA. In both cases strong screening is present in solution, the differences being that in region IIA we have a much higher monomer density than in region II. In region II the exponents in the relationships for $\langle s^2\rangle$ are very nearly

Table 1 Derived formulae for the behaviour of polymers in solution by use of scaling laws (*SL*) or mean-field theories (*MF*)

Region	$\langle s^2\rangle_{SL}$	$\langle s^2\rangle_{MF}$	ξ^2 *SL*	ξ^2 *MF*
I'	n	n	–	–
I	$n^{6/5}\beta^{2/5}$	$n^{6/5}\beta^{2/5}$	–	–
II	$n\rho^{-1/4}\beta^{1/4}$	$n\rho^{-1/5}\beta^{1/5}$	$\rho^{-3/2}\beta^{-1/2}$	$\rho^{-6/5}\beta^{-4/5}$
II A	–	$\langle s^2\rangle_0\,[1 + K\beta^{1/2}\rho^{-1/2}]$	–	$\rho^{-1}\beta^{-1}$
III	n	n	ρ^{-2}	–

Table 2 Molecular weights of PSH and PSD

Polymer	$10^{-4}\bar{M}_n$	$10^{-4}\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
PSH	4.70	6.11	1.29
PSD	4.90	7.57	1.54

identical and present experimental techniques are unable to discriminate between them.

The major difference is the region IIA, predicted by mean-field theory at high monomer density, the semi-concentrated region. This region has been partly investigated with regard to its excluded volume dependence in Part 1 of this series and the results were in excellent agreement with the theoretical formula. Here, we investigate this region further by examining the influence of concentration on the chain dimensions for the concentration range $40 \leqslant C$ (w/v %) $\leqslant 100$ and the influence of temperature on the screening length at a fixed concentration of polymer in the semi-concentrated region.

EXPERIMENTAL

Materials

Cyclohexane and deuterated cyclohexane (99.5 atom % D) were used without further purification. Hydrogenous polystyrene (PSH) and deuterated polystyrene (PSD) were prepared by anionic polymerization of their respective monomers in benzene using n-butyllithium as initiator. The polymers were characterized by gel permeation chromatography and the molecular weights so obtained are given in *Table 2*.

Solution preparation

Radius of gyration measurement. All solutions were made in a 19:1 (v/v) mixture of cyclohexane and deuterocyclohexane. This mixture was used since its coherent scattering length is equal in magnitude to that of PSH but of opposite sign; consequently there should be no measurable coherent neutron scattering from the PSH in solution. Polystyrene solutions were prepared covering the concentration range 55 to 95% (w/v). Each solution contained 2.5% (w/v) PSD, the balance being made up by PSH. All solutions were prepared 6 weeks before measurements were made and sealed into quartz cells which were held at 40°–45°C for the whole time preceding the experiments.

Screening lengths. For measurement of the temperature dependence of the screening length, hydrogenous polystyrene with a molecular weight ($\bar{M}_w$) of 1.02×10^5 was used. A 36% (w/v) solution was made in deuterated cyclohexane. The background solution used to measure the incoherent scattering was a mixture of deuterated and hydrogenous cyclohexane containing the same number of protons as the polymer solution.

Small-angle neutron scattering

Full discussions of theoretical and experimental details of small-angle neutron scattering (SANS) are available elsewhere and will not be given here[13–16].

Radius of gyration. Measurements of the scattered neutron intensity as a function of scattering vector, $Q[Q = (4\pi/\lambda)\sin(\theta/2)$, where λ = neutron wavelength and θ = scattering angle] were made on the D11 small-angle diffractometer at the Institute Laue–Langevin, Grenoble[17], France. An incident neutron wavelength of 10 Å was used and the sample–detector distance was such that $0.06 \leqslant 10^2 Q \leqslant 20$ (Å^{-1}). Polymer solutions were contained in cylindrical quartz cells with a 1 mm path length and equilibrated at the experimental temperature of 60°C for 48 h. The cells were then quickly transferred to a brass cell holder which was maintained at 60°C by a proportional controller. A thermocouple in the vicinity of the quartz cell recorded the temperature which was constant at 60° ±0.1°C.

After subtraction of background intensity (mainly incoherent scattering) the scattered neutron intensity was plotted according to the equation below:

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

where K^* is a constant. For concentrated solutions, A_2 in equation (1) is approximately zero[2] and consequently we have neglected this factor in the interpretation of the data.

Screening lengths. The polystyrene solution was contained in a quartz cell with a 2 mm path length. Measurements of scattered neutron intensity were made using the D17 diffractometer at the Institut Laue–Langevin[17]. An incident neutron wavelength of 11.6 Å was used and the sample detector distance was such that $1.8 \leqslant 10^2\ Q \leqslant 7.0$ (Å^{-1}). After subtraction of the background scattering, the scattered neutron intensity was interpreted using equation (2)[18]:

$$I(Q)^{-1} = (Q^2 + \xi^{-2})/f(T, c) \qquad (2)$$

where $f(T, c)$ describes a function which depends on the temperature and concentration of the solution but not on the scattering vector Q.

RESULTS

Radius of gyration

Figure 2 shows the total scattered neutron intensity from two polystyrene solutions at differing total concentrations and containing 2.5% PSD. Also shown is the scattered neutron intensity for a 95% solution of PSH in cyclohexane which does not show any Q dependence over the majority of the range investigated and is what would be expected from a purely incoherent scattering system.

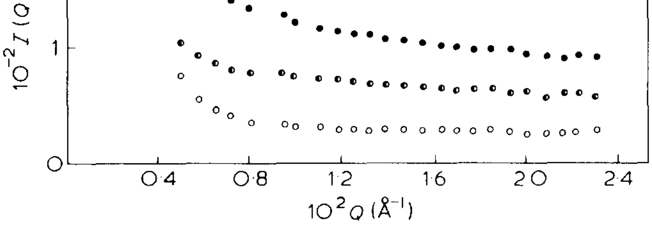

Figure 2 Total intensity of scattered neutrons [$I(Q)$] as a function of scattering vector (Q) for polystyrene solutions in cyclohexane. ○, 95% PSH; ◐, 58% total polymer – 2% PSD; ●, 95% total polymer – 2% PSD

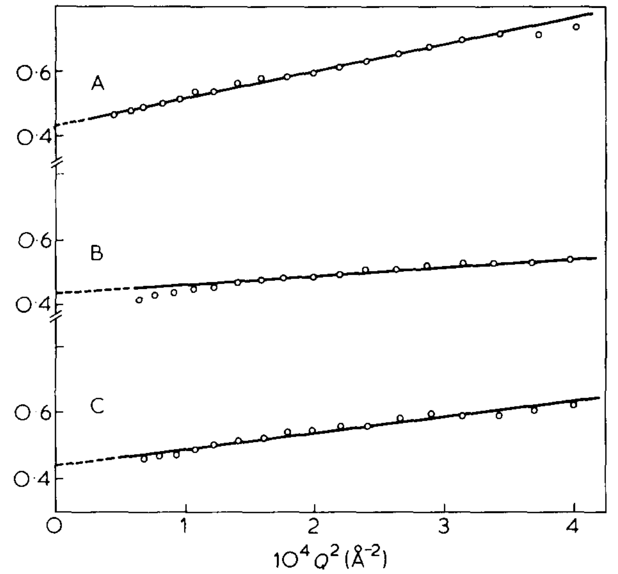

Figure 3 Zimm plots of the excess scattered neutron intensity for polystyrene in cyclohexane at 60°C: A, 95% total polymer; B, 75% total polymer; C, 58% total polymer

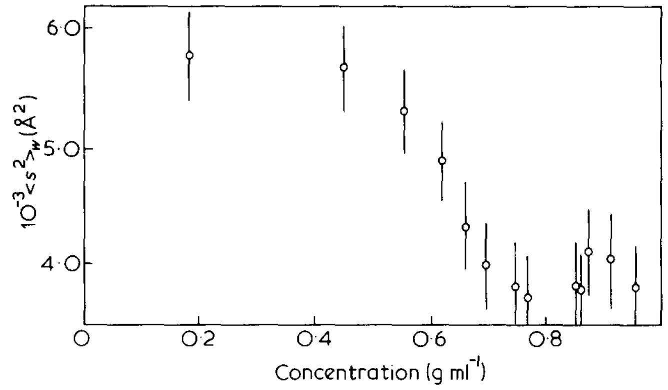

Figure 4 Dependence of mean square radius of gyration, $\langle s^2 \rangle_w$, on polymer concentration for polystyrene in cyclohexane at 60°C

However, a scattering contrast exists when deuterated polymer is present in solution, producing a coherent, Q-dependent signal superimposed on the Q-independent background. Typical plots of such data according to equation (1) are shown in *Figure 3*, the slope and intercepts being used to calculate the z-average mean square radius of gyration. Weight-average radii of gyration were obtained from the relation[19]:

$$\langle s^2 \rangle_w = \langle s^2 \rangle_w \frac{(h+1)}{(h+2)}$$

where

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

The dependence of radius of gyration on total polymer concentration is shown in *Figure 4* which includes earlier data obtained at lower concentrations.

Screening length

Typical plots of reciprocal scattered neutron intensity as a function of Q^2 are shown in *Figure 5*. At higher Q values the data follows a different scattering law. This is an example of a 'crossover' in the scattering law[20]. At higher values of Q the pair correlation function in the scattering law becomes dominated by excluded volume effects (since we now observe the chain at distances $\leqslant \xi$) and no longer follows the Lorentzian form of equation (2).

In these experiments we are essentially measuring the correlations between all monomer units since all chains are identical. Consequently the screening length, ξ, may be obtained in two ways. Firstly, from the slope and intercept of the data at low Q, since from equation (2)

$$\xi^{-2} = \text{Intercept/Slope}$$

Secondly, from the value of $Q(Q^*)$ where the crossover takes place:

$$\xi^{-1} = Q^*$$

We have only used the former of these methods due to the difficulty of obtaining Q^* accurately, especially at the higher temperatures. However, we note that the values of ξ obtained from Q^* show a similar trend as those described from the slope and intercept at lower Q, i.e. a decrease with increasing temperature. A plot of the screening length as a function of temperature is shown in *Figure 6*.

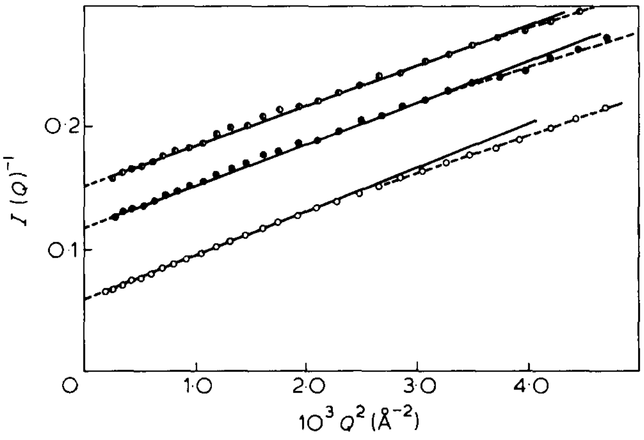

Figure 5 Reciprocal scattered neutron intensity as a function of the square of the scattering vector for polystyrene (PSH) in deuterocyclohexane. ◐, 54°C; ●, 46°C; ○, 31°C

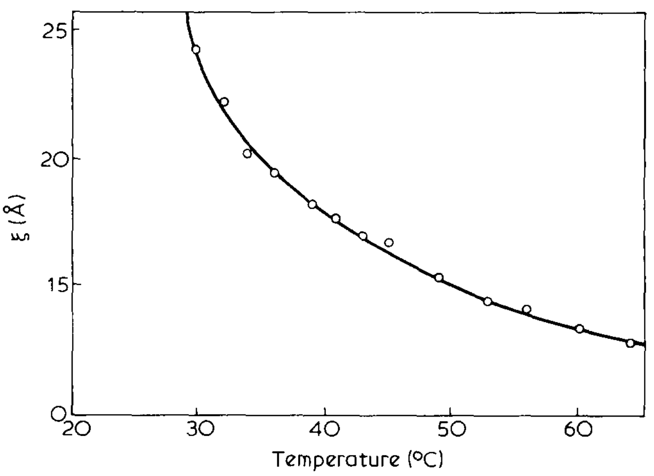

Figure 6 Dependence of screening length (ξ) on temperature for polystyrene in cyclohexane solution (36% polymer)

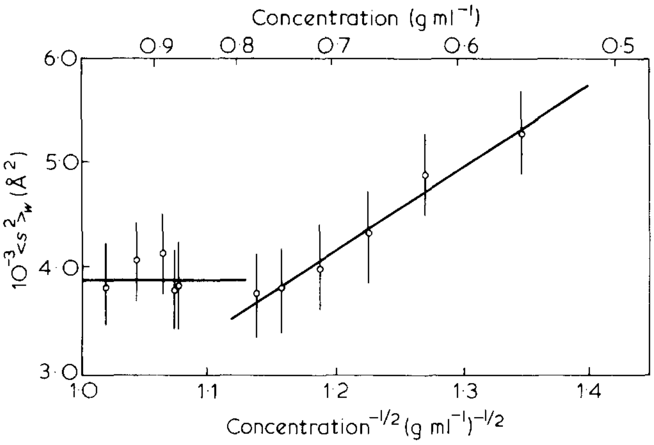

Figure 7 Mean square radius of gyration of polystyrene in cyclohexane at 60°C as a function of the reciprocal square root of total polymer concentration

DISCUSSION

Referring to *Table 1*, both radius of gyration and screening length are expressed in terms of the monomer density ρ. From the definition of ρ^4 we may express it in terms of the usual concentration units C (g ml^{-1}) i.e. $\rho = CN_A/m$, where N_A = Avogadro's number and m is the molecular weight of a monomer unit in the chain. Consequently, we can replace ρ by C in all the equations in *Table 1*, since this substitution will only alter the values of the constants. For the concentration range we are primarily concerned with here, the equations for region IIA in *Table 1* should apply. Substituting for ρ in the equation for the radius of gyration then

$$\langle s^2\rangle = \langle s^2\rangle_0(1 + K^1\beta^{1/2}C^{-1/2}) \qquad (3)$$

where $\langle s^2\rangle_0$ = Unperturbed mean square radius of gyration; and $K^1 = 4.6^{1/2}\ m^{1/2}/\pi l_0^3 N_A^{1/2}$ where l_0 = effective step length along the chain.

Clearly from equation (3) the mean square radius of gyration should have a linear dependence on $C^{-1/2}$ when we are in region IIA. A plot of the data according to equation (3) is shown in *Figure 7*. A linear dependence of $\langle s^2\rangle$ on $C^{-1/2}$ exists for the concentration range $0.5 \leqslant C$ (g ml^{-1}) $\leqslant 0.82$. At higher concentrations an approximately constant value of 3.9×10^3 Å^2 is obtained for $\langle s^2\rangle$. This value is somewhat lower than the unperturbed dimensions for a polystyrene molecule of the same molecular weight ($\langle s^2\rangle_0 = 4.24 \times 10^3$), but is within error. Notwithstanding this, it is apparent that the formula is a good description of the dimensions in a semi-concentrated solution and that unperturbed dimensions are obtained for $C > 0.82$ g ml^{-1}.

Apart from the concentration, the other major variable which influences the observable properties is the excluded volume, β. No exact form exists for this parameter but it has been shown that it is influenced by the solvent used and the temperature in any particular solvent. Frequently, the temperature variation of the excluded volume is approximated by:

$$\beta \propto (T - \theta)$$

which is obeyed at temperatures not too distant from θ. [We note also that renormalization group theory of magnetic systems uses a reduced temperature variable of $(T - T_c)/T_c$ where T_c is a critical temperature.]

We therefore replace β in *Table 1* by $(T - \theta)$. If the solution is semidilute then as the temperature increases from θ, ξ^2 should not change over a limited temperature range corresponding to region I′, the theta region. Outside this region ξ^2 should change with temperature. This behaviour has been observed by other workers from log-log plots of ξ^{-2} as a function of $(T - \theta)$[6]. If the data of *Figure 6* is plotted in this manner a continuously curved plot is obtained from which no limiting slope is obtained. In the semi-concentrated regime, the screening length is given by:

$$\xi^2 = \frac{l l_0}{6\rho\beta}$$

where l is a 'perturbed' step length, near the θ temperature $l \approx l_0$, hence:

$$\xi^2 \simeq \frac{l_0^2}{6\rho(T - \theta)}$$

and a plot of ξ^{-2} should be linear in $(T - \theta)$. This plot is shown in *Figure 8* where we have used $\theta = 40.2$°C in accordance with experimental results of Strazielle[21], and is indeed linear over the temperature range studied. A linear dependence of ξ^{-2} is also obtained below the theta temperature which is in accordance with the results of $\langle s^2\rangle$ presented in Part I of this series.

CONCLUSIONS

We have obtained data from small-angle neutron scattering experiments on polystyrene in cyclohexane which give further support to additional behaviour regimes existing as well as those predicted by renormalization group theory. The variation of radius of gyration with concentration (fixed temperature) and screening length with temperature (fixed concentration) agree with predictions based on a theory derived by Edwards and Jeffers[4]. A cautionary note should be made here: whatever theoreti-

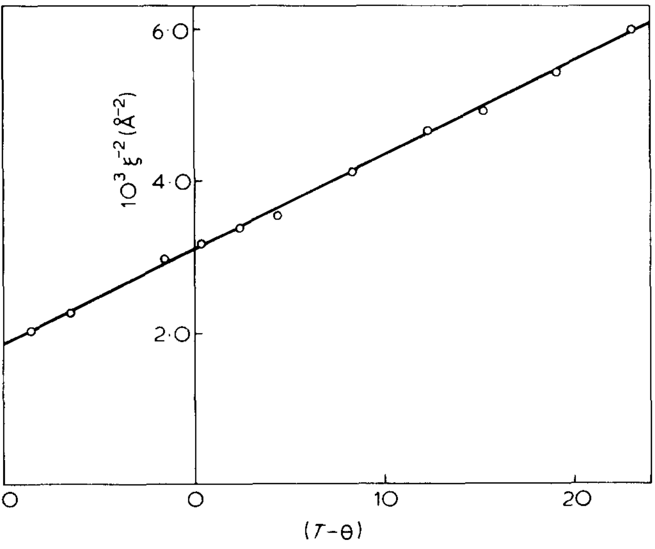

Figure 8 Reciprocal squared screening length (ξ^{-2}) dependence on temperature

cal approach is used the properties of the polymer in solution are a function of the four variables noted earlier. The excluded volume and concentration dependences are inextricably linked and cannot be completely separated from each other. Thus, as the temperature is changed the monomer density changes, due to volume changes, as well as the excluded volume β. As the concentration is altered the influence of the excluded volume is altered due to the change in the number of intermolecular contacts. Consequently the agreement with theory that we have observed may be fortuitous. The theoretical formulae should only apply in the near neighbourhood of the theta temperature, i.e. where the excluded volume is not strong[22]. The maximum value of the mean square radius of gyration we observe here is $\sim 5.77 \times 10^3$ Å^2 which corresponds to an expansion factor (α) of 1.17, i.e. a weak excluded volume effect and this may be the reason for the agreement between theory and experiment that is observed.

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