Temperature dependence of chain dimensions

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(Received 8 August 1977)

The dimensions of linear atactic polystyrene ($\bar{M}_w$ = 75 700) in cyclohexane have been determined at a series of temperatures using small-angle neutron scattering. Three solutions were examined: dilute (2% polymer), semi-dilute (19% polymer) and concentrated (47% polymer). End-to-end distances obtained from the data were compared with current theories of polymer solutions. For the semi-dilute solution results agreed with scaling law predictions, whereas results from the concentrated solution agreed with the formula obtained by Edwards. Furthermore, the latter results gave a characteristic ratio (C_∞) of 9.5 ± 0.7 for polystyrene.

INTRODUCTION

Dilute solution properties of polymers are usually described by the two parameter theory[1]. One of these parameters, the unperturbed dimension can now be accurately calculated using rotational isomeric state methods developed by Flory and collaborators[2], provided the statistical weights of the rotamers can be assigned. The excluded volume parameter, z, continues to be the subject of much theoretical discussion. Many expressions have been derived relating polymer chain expansion to z[1]. Such expressions are summarized by the relationship between end-to-end dimensions, r^2, and degree of polymerization, N, derived by Monte Carlo methods for a chain on any lattice[3]:

$$r^2 = N^{\upsilon}$$

where $\upsilon \sim 6/5$. Edwards[4], subsequently obtained in the limit of infinitely long chains, $\upsilon = 6/5$, using an analytical method.

Recent developments in the theory of polymer solutions, at concentrations greater than the usual dilute limits, stem from the use of mean field theory techniques by Edwards[5]. He showed that in these more concentrated solutions the excluded volume becomes of lesser importance due to the screening effect of segments from neighbouring chains. More recently, an alternative approach has used magnetic systems as analogues for polymer solutions[6,7]. Application of scaling law techniques resulted in a free energy expression somewhat different to that of Edwards. On the basis of this theory and using the correspondence between a magnetic tricritical point and the theta temperature of a polymer solution[8], Daoud and Jannink[9] have obtained relationships between various polymer solution properties and concentration and temperature. At the same time Edwards[10] derived an equation relating $\langle r^2\rangle$ to the temperature and concentration of solutions for the intermediate and concentrated ranges.

This paper describes results of small-angle neutron scattering on dilute, semi-dilute and concentrated solutions of polystyrene in cyclohexane over a range of temperature. Interpretation is made in the light of the various theoretical expressions now available.

THEORY

Polymer chain dimensions are influenced by temperature in two ways: (a) by changing the population of *trans*/*gauche* conformations of chain segments leading to the temperature coefficient of unperturbed dimensions, $\mathrm{d}\ln r_0^2/\mathrm{d}T$. We will not be concerned with this here, its influence being negligible; (b) by the change in excluded volume with temperature, generally described (in the region of the theta temperature, θ) by equation (1):

$$V = B_0(1 - \theta/T) \qquad (1)$$

where V is the excluded volume per monomer segment. This equation is the basis for the temperature dependences predicted by scaling laws and analytical formulae.

Daoud and Jannink[9], on the basis of scaling laws, divide the temperature–concentration diagram for polymer solutions into lower regions of distinct behaviour. Such a diagram is given in *Figure 1*, plotted using their data and the relationships derived by theory. The effect of molecular weight is removed by multiplying abscissa and ordinate by $M_w^{1/2}$. In *Figure 1*, region I, the dilute solution regime, is bound by $CM^{1/2} = 0$ and the line $C^*M^{1/2} \simeq (\theta_T M^{1/2})^{-3/5}$. Region II, bound by C^*M and a line $C^{**}M^{1/2} \simeq \theta_T M^{1/2}$ is the semi-dilute region wherein polymer molecules are overlapping to

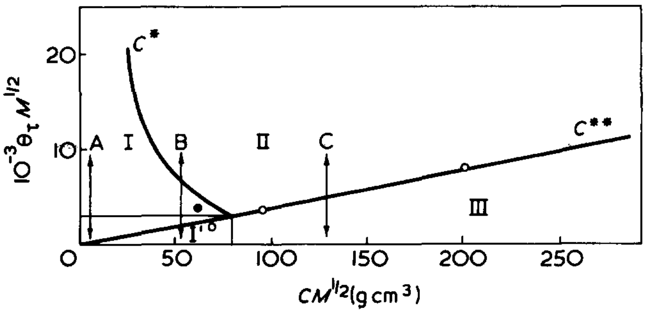

Figure 1 Temperature–concentration diagram for polymer solutions $\theta_T = (T - \theta)$, △, ○, from ref 11. Lines A, B, and C correspond to dilute, semi-dilute and concentrated solutions and temperature ranges studied here

Table 1 Radius of gyration, $\langle s^2 \rangle$, relationships predicted by theory

Region	$\langle s^2 \rangle$ Scaling laws	$\langle s^2 \rangle$ Edwards
I	$N^{6/5}\theta_T{}^{2/5}$	$N^{6/5}\theta_T{}^{2/5}$
I′	N	–
II	$Nc^{-1/4}\theta_T{}^{1/4}$	$[C_\infty n l^2(1 + K\theta_T{}^{1/2})]/6$
III	N	

a small extent. Overlap begins at the concentration C^* which is approximately $(3\bar{M}_w/4\pi N_A\langle s^2\rangle_w{}^{3/2})$. Region III is the concentrated solution regime, between $C^{**}M$ and $\theta_T M^{1/2} = 0$. Finally the tricritical region I′ lies in the immediate neighbourhood of the θ point ($\theta_T = 0$) wherein no dependence of polymer chain dimensions on temperature is predicted.

For each of these regions, the dependence of the radius of gyration on polymer concentration and temperature (θ_T) is set out in *Table 1* as determined by scaling laws and the analytical theories of Edwards[4,10]. Clearly, in the semi-dilute and especially the concentrated solution regions, markedly different temperature dependences are forecast.

We have made measurements of $\langle s^2\rangle_w$ in each of the three concentration regimes I, II and III. The actual ranges covered are shown by the lines A, B and C drawn on *Figure 1*, all of them cross at least one behaviour boundary. More detailed measurements in the semi-dilute region have been made recently by Cotton *et al.* Such measurements of $\langle s^2\rangle_w$ for polymers in solutions with concentrations outside the usual dilute limit (≈1% w/v), may easily be made by small-angle neutron scattering. In this technique, a few deuterated chains are dispersed amongst the remaining hydrogenated chains and solvent which make up the solution. Due to the different coherent scattering lengths of deuterium ($b_{\mathrm{coh}} = 0.67 \times 10^{-12}$ cm) and hydrogen ($b_{\mathrm{coh}} = -0.37 \times 10^{-12}$ cm), a contrast is developed generating measureable neutron scattering from which $\langle s^2\rangle_w$ can be calculated. Further details on the technique are provided in the literature[12].

EXPERIMENTAL

Materials

Cyclohexane and deuterated cyclohexane (C_6D_{12}, 99.5% D) were used without further purification. Hydrogenous polystyrene (PSH) and deuterated polystyrene (PSD) were prepared from their respective monomers by anionic polymerization. Molecular weights were determined by gel permeation chromatography (courtesy of Mr D. Roy, Manchester University), values of $\bar{M}_n$ and $\bar{M}_w$ so obtained are given in *Table 2.*

Solutions and temperature range

The dilute solution contained 1.8% w/v of PSD in cyclohexane (C_6H_{12}). At this concentration no molecular overlap is present and intermolecular interference effects on the observed neutron scattering are negligible. For the semi-dilute solution a total polymer concentration of 19% w/v was chosen because it covered both regions I′ and II in *Figure 1.* The PSD concentration was 2.5%. A concentrated solution was also prepared from a mixture of the two polymers such that the total polymer concentration was 47% and PSD concentration 2.0% (both w/v). For the semi-dilute and concentrated solutions the solvent was a C_6H_{12}/C_6D_{12} mixture (19:1 v/v) wherein the coherent neutron scattering contrast between PSH and solvent was zero.

Determination of the radius of gyration

The radius of gyration can be obtained by plotting the scattered neutron intensity according to the Zimm equation:

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

where $I(Q)$ is the intensity of neutrons scattered at scattering vector Q [$=(4\pi/\lambda)\sin\theta/2$], A_2 is the second virial coefficient and $\langle s^2\rangle_z$ the z-average mean square radius of gyration. K^* is a constant composed of instrumental parameters and other factors. Scattered neutron intensities were measured using the D11 small-angle neutron diffractometer[13] at the Institut Laue–Langevin, Grenoble, France. The range of scattering vector was $0.4 \leqslant 10^2 Q \leqslant 2.2$ Å^{-1}, corresponding to the Guinier region ($Q\langle s^2\rangle_z^{1/2} \leqslant 1$) in which equation (2) is applicable. $I(Q)$ relates to the scattering of the PSD molecules alone and is obtained by subtracting the scattered intensity of a PSH solution from that of the PSD/PSH mixture in solution, PSH concentrations being equal in both cases. For the dilute solution the background scattering was that of C_6H_{12} alone. For this case A_2 in equation (2) is the commonly encountered parameter characterizing polymer–solvent interactions. In both the semi-dilute and concentrated solutions, A_2 refers to PSD–PSH interactions. This has been found to be zero for PS dissolved in good solvents[11] and we have disregarded this factor here.

Both solutions and backgrounds were contained in silica cells with a 1 mm path length which were mounted in brass holders wound with heating wire. Temperature control was maintained via a proportional controller connected to a platinum resistance thermometer in the immediate vicinity of the cell. A thermocouple, also in the cell compartment recorded the temperature. Temperatures between 32° and 65°C were maintained to ±0.05°C.

RESULTS

Scattered neutron intensities at temperatures of 32° and 65°C are shown in *Figure 2* for the concentrated PSD–PSH solution in cyclohexane. Also shown is the scattered intensity for the background solution (45% PSH in C_6H_{12}/C_6D_{12} mixture), which is approximately constant over the whole range of Q. By contrast, scattering from the PSD–PSH mixture is dependent on Q. In both cases the increase in intensity below $Q = 0.7 \times 10^{-2}$ Å^{-1} ($\theta \approx 0.6°$) is attributable to incident beam contamination. The scattered intensity from the backgrounds were not markedly temperature dependent, consequently scattered background intensities measured at the median temperature of 50°C were used. After subtraction of appropriate backgrounds and corrections for transmittances etc., the data was plotted according to equation (2) ($A_2 = 0$). Typical plots are shown in *Figure 3.* Values

Table 2 G.p.c. molecular weights of polystyrenes

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

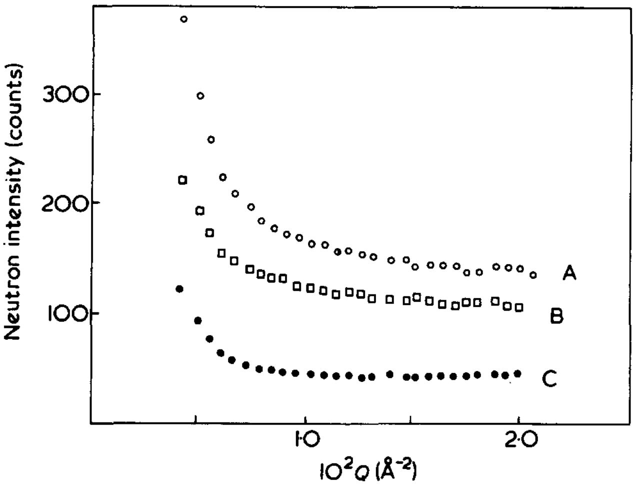

Figure 2 Scattered neutron intensities for the concentrated PSD/PSH solution at: A, 65°C; B, 32°C and C, PSH background solution at 50°C

of $\langle s^2\rangle_z$ were calculated from these plots and subsequently corrected to the $\langle s^2\rangle_w$ values in *Table 3.*

Additionally, for the concentrated solution, a few measurements were made at temperatures which were some 20° *below* the theta temperature for this system (30°C *vide infra*). No difficulties were encountered in these measurements. Qualitative evidence for incipient precipitation at the lowest temperature (10°C), was the increase in scattered neutron intensity from background and sample solutions. These data are given in *Table 4.*

DISCUSSION

Dilute solution

Although the dimensions of polymers in solution may increase or decrease on heating[14], it is known from dilute solution measurements that an increase is observed for polystyrene in cyclohexane[15] and similar theta solvents[16]. The results obtained here appear to contradict these well-established experimental data, showing a decreasing trend with increasing temperature. This can be accounted for by the neglect of A_2 in equation (2), especially at high temperatures. It can be shown that:

$$\langle s^2\rangle_{\text{true}} = \langle s^2\rangle_{\text{abs}}\,(1 + 2A_2M_wC)$$

where $\langle s^2\rangle_{\text{true}}$ is the mean square radius of gyration in the absence of excluded volume effects; $\langle s^2\rangle_{\text{abs}}$ is the mean square radius of gyration determined from the plots of *Figure 3* and A_2 is the second virial coefficient of the system. C and M_w retain their usual meanings.

Values of $\langle s^2\rangle_{\text{true}}$ were calculated using values of A_2 interpolated from data of Krigbaum[17] and are plotted against temperature in *Figure 4.* We do not attempt to analyse the data further, suffice to say that corrected values of $\langle s^2\rangle_w$ behave qualitatively in the *a priori* expected manner. What is clear is that the dilute solution data, even before correction show markedly different behaviour to that of the semi-dilute and concentrated solutions discussed below.

Semi-dilute solution

From the scaling law equation for region II given in *Table 1*, it is clear that a value for the theta temperature of PSD in cyclohexane is required. It has been found that this temperature is 30°C[18], approximately 5° lower than that of PSH in cyclohexane. To check whether the present system has the same theta temperature we have plotted in *Figure 5* $\langle s^2\rangle_w^4$ as a function of temperature since

$$\langle s^2\rangle_w^4 \approx N^4C^{-1}(T-\theta) \tag{3}$$

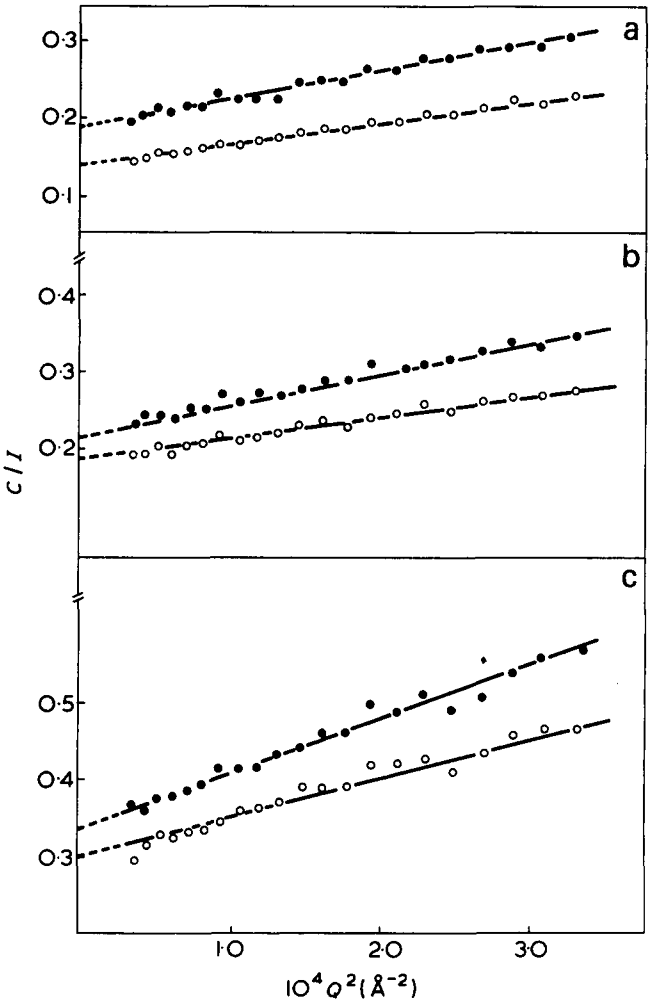

Figure 3 Zimm equation plots (A_2 = 0) for (a) dilute, (b) semi-dilute and (c) concentrated solutions of polystyrene in cyclohexane. ○, 32°C; ●, 65°C

Table 3 Weight-average mean square radii of gyration of polystyrene in cyclohexane determined by small-angle neutron scattering

	$10^{-3}\langle s^2\rangle_w$(Å^2)		
Temperature (°C)	Concentrated solution	Semi-dilute solution	Dilute solution
32	5.43 ± 0.4	4.79 ± 0.3	5.85 ± 0.3
34	5.65 ± 0.4		
36	5.72 ± 0.4	4.85 ± 0.3	5.68 ± 0.3
38	5.70 ± 0.4		
40	5.96 ± 0.4	4.84 ± 0.3	5.47 ± 0.3
42	6.12 ± 0.4		
44	5.99 ± 0.4	4.96 ± 0.3	5.53 ± 0.3
46	6.24 ± 0.4		
50	6.17 ± 0.4	5.12 ± 0.3	5.56 ± 0.3
55	6.42 ± 0.4	5.35 ± 0.3	5.50 ± 0.3
60	6.96 ± 0.4	5.76 ± 0.3	5.30 ± 0.3
65	6.75 ± 0.4	6.06 ± 0.3	5.29 ± 0.3

Table 4 Weight-average mean square radius of gyration of polystyrene in concentrated cyclohexane solution, for temperatures below θ

Temperature (°C)	$10^{-3}\langle s^2\rangle_w$(Å^2)
32.0*	5.45 ± 0.4
28.0	4.77 ± 0.4
20.0	4.26 ± 0.4
14.5	4.16 ± 0.4
10.0	3.80 ± 0.4

* Redetermination i.e. not determined at the same time as that given in *Table 3.*

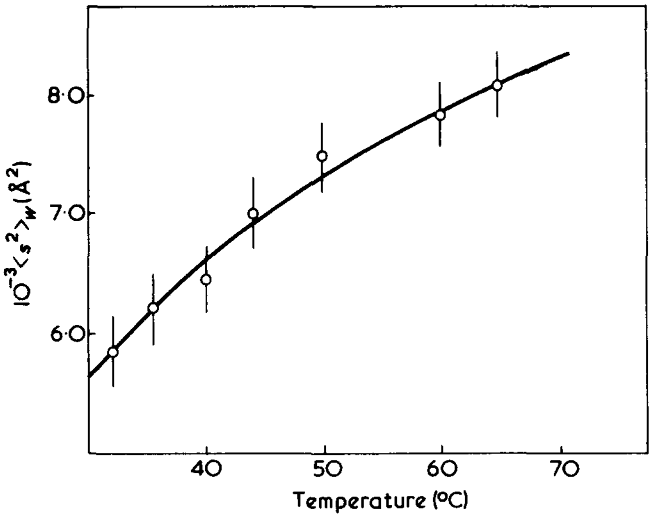

Figure 4 $\langle s^2\rangle_w$ of PSD in dilute cyclohexane solution after correction for A_2 dependence

and at $\langle s^2\rangle_w^4 = 0$, $T = \theta$. Although plotting the results in such a form magnifies experimental errors present, extrapolation of the results from $T \geqslant 44$°C to $\langle s^2\rangle_w^4 = 0$ gives a theta temperature of 31.5°C, a value which is in reasonable agreement with the aforementioned accurately determined value of 30°C which will be used in subsequent interpretation.

Referring to *Figure 1,* we see that for a semi-dilute solution (line B), at low temperatures (region I′) $\langle s^2\rangle_w$ should be independent of temperatures, at higher temperatures the behaviour predicted by the scaling law equation should be observed. *Figure 5* shows that this is indeed a description of the experimental behaviour. Up to ~44°C $\langle s^2\rangle_w$ is approximately independent of temperature, thereafter being dependent. The slope of the temperature-dependent portion of the log–log plot in *Figure 5* is 0.26 ± 0.05, a result in agreement with that predicted by the scaling law equation in *Table 1.* All of these results confirm the much more detailed results of Cotton *et al.*[11] and provide a contrast with the data of the succeeding section.

Concentrated solution

For this solution, scaling laws predict no temperature dependence whilst Edwards[10] predicted a dependence on $(T-\theta)^{1/2}$. Line C in *Figure 1* pertains to the measurements made by us. Initially at low temperatures the solution is in the concentrated region, eventually becoming semi-dilute at $\theta_T M^{1/2} \approx 5 \times 10^3$ ($\equiv T \approx 50$°C). The Edwards equation can be written in terms of the end-to-end distance, $\langle r^2\rangle_w$, as

$$\langle r^2\rangle_w = C_\infty n l^2[1 + a_0\omega^{-1/2}\rho^{-1/2}(T-\theta)^{1/2}] \qquad (4)$$

where n is the number of bonds of length l in a polymer chain whose characteristic ratio is C_∞, $a_0 = 2\sqrt{3}/\pi l^{5/2}$, ω contains thermodynamic parameters and ρ is proportional to the number density of polymer chains in the solution. The linear dependence of $\langle r^2\rangle_w$ on $(T-\theta)^{1/2}$ forecast by equation (4) is admirably displayed in *Figure 7* for temperatures above and below θ. Moreover, there seems to be no departure from this behaviour at $T \geqslant 50$°C. Furthermore, from the extrapolated intercept at $(T-\theta)^{1/2} = 0$ of *Figure 7,* using $l = 1.54$ Å C_∞ is calculated to be 9.5 ± 0.7 which is in excellent agreement with the value of 10.0 derived from dilute solution viscosity data.

Plotting these same data as in *Figure 5,* i.e. as if semi-dilute, results in a shallow curve from which no limiting slope can be obtained. Conversely, plotting the data obtained from the 19% semi-dilute solution according to equation (4), also results in a curved plot with no limiting slope.

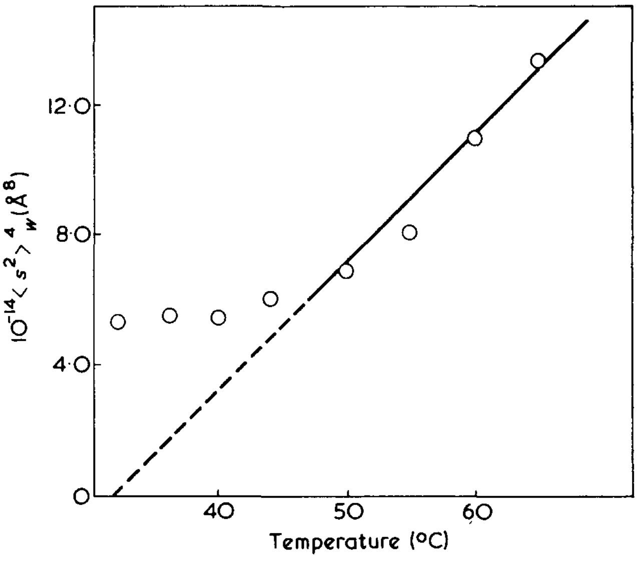

Figure 5 $\langle s^2\rangle_w^4$ as a function of temperature for the semi-dilute solution

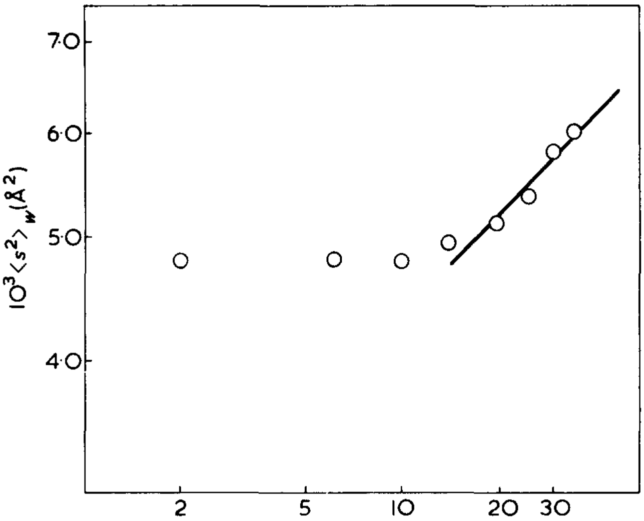

Figure 6 Log–log plot of $\langle s^2\rangle_w$ as a function of $(T-\theta)$ for the semi-dilute solution

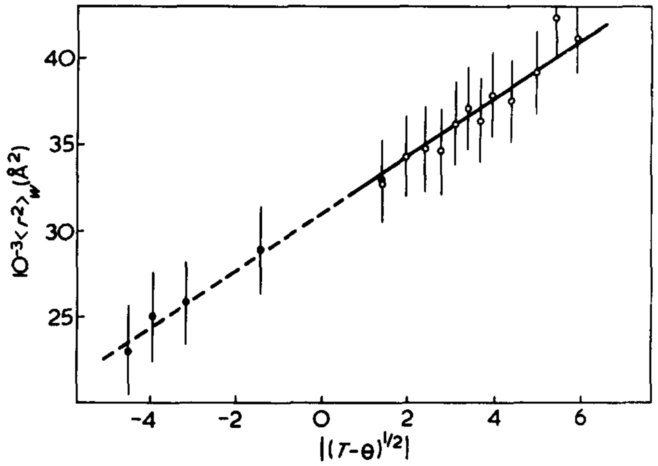

Figure 7 End-to-end distance of polystyrene in concentrated solution, dependence on $|(T-\theta)^{1/2}|$. ○, values for 32° < T < 65°C; ●, values for 10° < T < 32°C

CONCLUSIONS

Since it is clear that A_2 is influencing the results for the dilute solutions, we limit our remarks to chain dimensions in the semi-dilute and concentrated solutions.

Our results for the semi-dilute solution are essentially in agreement with the more detailed results of Cotton *et al.* reported elsewhere[11]. The initial linear part corresponds to the tricritical region discussed by de Gennes, and indeed $\langle s^2\rangle_w$ here is quite close to the expected unperturbed value of $\approx 5 \times 10^3$ Å^2.

On the other hand, the concentrated solution appears to behave exactly as predicted by Edwards in the semi-dilute and concentrated solutions. The extension of this equation into the semi-dilute regime underlines the idealized nature of *Figure 1*, which implies sharp divisions between each region. Regions II and III are more likely to have a diffuse boundary, since at $T \gg \theta$, the potential describing the excluded volume includes terms other than the hard core repulsion implicit in the $(T-\theta)$ temperature dependence[19]. More important is the temperature dependence observed in the concentrated region which raises questions about the general applicability of the scaling law techniques. According to Edwards the important physical factor in the applicability of equation (4) is that the volume occupied by a chain (V_0) should be much greater than the volume of solvent per chain (V_c). For the concentrated solution $(V_0/V_c) \approx 23$ and so fulfils the above condition. Surprisingly, for the semi-dilute solution $(V_0/V_c) \approx 9$, a figure not significantly different from that of the concentrated solution. Clearly, chain dimensions are extremely dependent on this ratio. Conceivably at temperatures approaching the lower critical solution temperature, the concentrated solution may display semi-dilute behaviour due to the greater solvent expansion.

It is apposite here to make a few comments regarding the extension of equation (4) into a $T < \theta$ region as shown in *Figure 7.* Equation (4) becomes indeterminate in such regions and moreover the polymer is expected to precipitate out. There appear to be two reasons for the observed behaviour: (i) on a practical level, for molecular weights less than infinity, precipitation takes place at $T < \theta$; (ii) scaling laws identify the line $\theta_T M^{1/2} = 0$ in *Figure 1* as a line of symmetry for the Gaussian behaviour of the chain[9], and the line $C^{**}(-\theta_T)$ symmetrical to $C^{**}(\theta_T)$ in *Figure 1* is one of the asymptotes of the precipitation curve. Between these two lines the same behaviour would be expected, a change of sign being necessary on crossing the $\theta_T M^{1/2} = 0$ line to maintain symmetry.

In an attempt to answer the questions posed by the scaling law equation in region II of *Figure 1* and equation (4), this paper has raised several more.

(1) Equation (4) predicts a (concentration)$^{-1/2}$ dependence of chain dimensions in the concentrated region. This is not predicted by the scaling laws.

(2) In the bulk state polymer chains attain their unperturbed dimensions and consequently have a very small temperature dependence. At some concentrations in excess of the highest studied here a very much smaller temperature coefficient of chain dimensions should be observed. An indication of the concentration regime may be given by the extrapolation formula for polymer dimensions at present being developed by Edwards and Jeffers[20].

(3) All the results gathered so far have been in the region of the upper critical solution temperature and have been implicitly developed from enthalpic considerations. We have mentioned above the possibility of a change in behaviour at the lower critical solution temperature where the enthalpic criterion changes sign.

We hope to clarify these points in future experiments.

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