Second and Third Virial Coefficients for Polystyrene in Cyclohexane near the Θ Point

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ABSTRACT: Second and third virial coefficients (A_2 and A_3) for six polystyrene fractions ranging in weight-average molecular weight (M_w) from 2×10^4 to 3×10^6 in cyclohexane were determined by light scattering at different temperatures (T) between 27 and 45 °C. The Θ point where A_2 vanishes was 34.5 °C (±0.3 °C) independent of M_w above 5×10^4. The curve of A_3 vs T obtained for each fraction was nearly parabolic with a broad, positive minimum around Θ, and the minimum became very shallow as M_w decreased. The values of A_3 at Θ were 6.5 (±2.5) × 10^{-4} mol g^{-3} cm^6 depending slightly on M_w and thus demonstrated the breakdown of the binary-cluster approximation at least to A_3 at the Θ point. It was found that the currently available first-order perturbation theories of A_2 and A_3 for linear flexible chains with three-body segment interactions fail to give a consistent explanation of the molecular weight independent Θ (for M_w above 5×10^4) and the positive A_3 values at the Θ temperature.

Introduction

In previous work,[1,2] we determined third virial coefficients (A_3) for polystyrene fractions in benzene from light-scattering measurements, using the Bawn plot[3] of $S(c_1,c_2)$ vs $c_1 + c_2$ based on the expression

$$S(c_1,c_2) \equiv [(Kc/R_0)_{c=c_2} - (Kc/R_0)_{c=c_1}]/(c_2 - c_1) = 2A_2 + 3A_3(c_1 + c_2) + 4A_4(c_1^2 + c_1c_2 + c_2^2) + \ldots \quad (1)$$

Here, K is the optical constant, c is the polymer mass concentration, R_0 is the reduced scattering intensity at zero scattering angle, c_1 and c_2 are different c values, and A_2 and A_4 are the second and fourth virial coefficients, respectively. In the present study, the measurement was extended to cyclohexane solutions of the polymer to determine A_3 near or at the Θ point where A_2 vanishes. In this regard, the following remark may be in order.

Two-parameter theories[4] predict that A_3 for linear flexible chains should vanish at Θ. Though not definitive, a few pieces of experimental evidence against this prediction are available in the literature.[5-7] Since a nonvanishing $A_3(\Theta)$ (=A_3 at Θ) implies that three-body segment interactions remain nonzero at the Θ point, unambiguous determination of $A_3(\Theta)$ should enable us to judge the validity of the two-parameter model for A_3 under the Θ condition.

Experimental Section

Six polystyrene fractions with molecular weights of 2×10^4–3×10^6 were used for the present study. One of them, designated below as F′4-B, was the central fraction obtained from Toso's standard "monodisperse" sample F4 by fractional precipitation with benzene as the solvent and methanol as the precipitant. The other five fractions, 2b-B, 4a-B, F-40B, F80-B, and F288-B, were chosen from the previously investigated samples.[1,2]

Seven cyclohexane solutions with different polymer weight fractions were prepared for each fraction. Scholte's data[8] for the solution density were used to calculate c; desired densities at different temperatures were obtained by interpolation or extrapolation of his data. The highest c studied for a given fraction was 2–4 times as high as that in our previous work[1,2] on benzene solutions.

Light-scattering measurements were made at different temperatures between 27 and 45 °C on a Fica 50 light-scattering photometer with vertically polarized incident light of 546-nm wavelength in an angular range from 15 to 150°. The scattering intensity data obtained were extrapolated to zero angle, using Berry's square-root plot[9] of $(Kc/R_\theta)^{1/2}$ vs $\sin^2(\theta/2)$, where R_θ denotes the reduced scattering intensity at a scattering angle θ. For specific refractive index increments, Scholte's data[8] were used.

Results and Discussion

Data Analysis. Figure 1 illustrates the concentration dependence of Kc/R_0 for 4a-B in cyclohexane at the indicated temperatures. The curves fitting the data points at the respective T bend upward and appear to converge to a common intercept. The Bawn plots constructed from these data are shown in Figure 2. The plotted points at any T follow a straight line, whose intercept and slope may be equated to $2A_2$ and $3A_3$, respectively, according to eq 1. Similar plots for six polystyrene fractions at a fixed T of 34.5 °C are displayed in Figure 3.

With A_2 and A_3 evaluated for a given fraction at each T, an apparent molecular weight (M_{app}) defined by

$$M_{app} = [(Kc/R_0) - 2A_2c - 3A_3c^2]^{-1} \quad (2)$$

was calculated as a function of c. Figure 4 shows that the resulting plots of M_{app} vs c for the six fractions at 34.5 °C are horizontal and permit unambiguous determination of M_{app} at infinite dilution, i.e., the weight-average molecular weights of the respective fractions. The values of M_w obtained at 34.5 °C agreed with those at other temperatures within ±1% for any fractions. They are presented in Table I, along with the previous M_w data[1,2] in benzene. The M_w values in the two solvents are seen to agree within ±2.5%, especially within ±1% for fractions 4a-B, F-40B, and F80-B.

Second Virial Coefficient and Θ Temperature. Figure 5 depicts the temperature dependence of A_2 for the six fractions in cyclohexane. Except for the lowest molecular weight fraction 2b-B, A_2 becomes zero at 34.5 °C (±0.3 °C); the graphically estimated A_2 value for the highest molecular weight fraction F288-B is 2×10^{-6} mol g^{-2} cm^3 (see Figure 3), but it cannot be distinguished from zero. Miyaki et al.[10,11] showed that A_2 of polystyrene in cyclohexane vanishes at the same T of 34.5 °C for M_w ranging from 1.9×10^5 to 5.6×10^7. Thus, it seems reasonable to conclude that, above $M_w \sim 5 \times 10^4$, Θ for the polystyrene–cyclohexane system is virtually independent of molecular weight. This disagrees with the finding of Vink[6] whose osmotic pressure data for the same system showed Θ to increase appreciably with decreasing molecular weight. Our A_2 data at 34.5 °C are presented in the third column of Table I.

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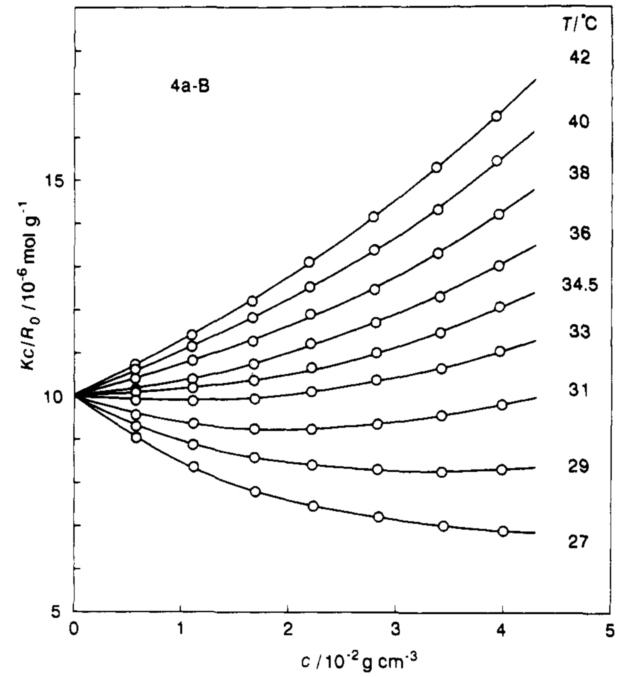

Figure 1. Concentration dependence of scattering intensity at zero angle for polystyrene fraction 4a-B in cyclohexane at indicated temperatures.

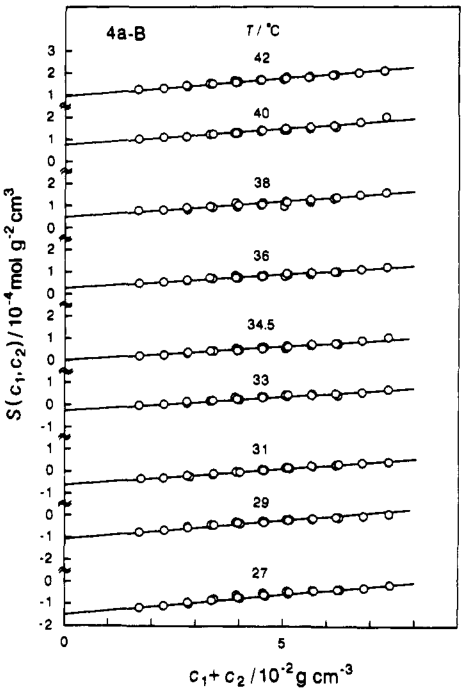

Figure 2. Bawn plots constructed from the data in Figure 1.

Recently, Huber and Stockmayer[12] found that A_2 for low molecular weight polystyrene ($M_w \lesssim 10^4$) in cyclohexane at 35 °C is positive and markedly increases with decreasing M_w (in their work, this temperature is the Θ point for high molecular weight samples). Their A_2 value for a sample with $M_w \sim 10^4$ is about 10^{-5} mol g^{-2} cm^3, which is comparable to ours at 34.5 °C for the lowest molecular weight fraction 2b-B ($M_w \sim 2 \times 10^4$, see Table I). Thus, Θ should begin to decrease from the Θ point for high molecular weight samples at a certain M_w between 2×10^4 and 5×10^4.

Third Virial Coefficient. The temperature dependence of A_3 is shown in Figure 6. The curve for each fraction is nearly parabolic with a broad minimum around 34.5 °C, and the minimum becomes very shallow as M_w decreases. This molecular weight dependent variation in A_3 with T is probably the first finding and awaits some theoretical interpretation. Another point to be made is that A_3 for any fraction remains nonzero at Θ. This reveals the breakdown of the two-parameter theory for A_3 near the Θ point; the theory predicts that A_2 and A_3 simultaneously vanish when the binary cluster integral becomes zero.

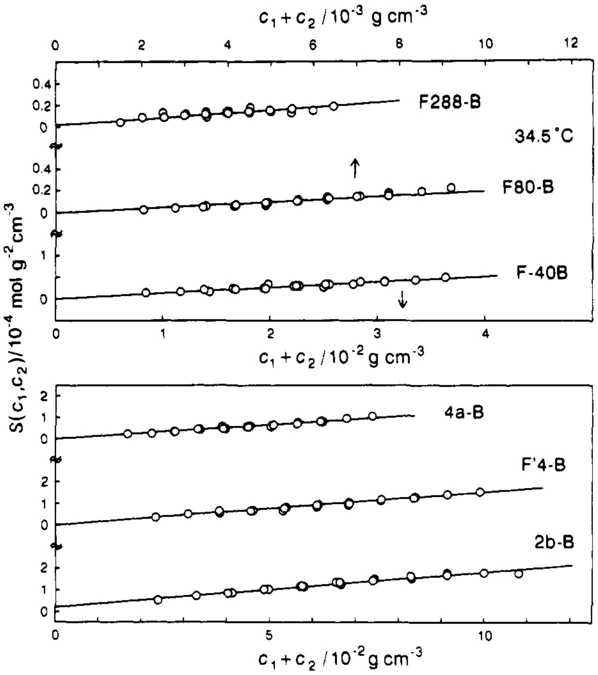

Figure 3. Bawn plots for six polystyrene fractions in cyclohexane at 34.5 °C.

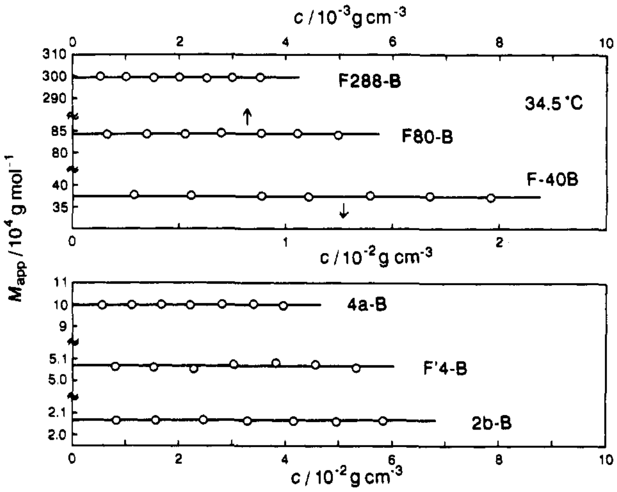

Figure 4. Plots of M_{app} vs c for polystyrene fractions in cyclohexane at 34.5 °C. M_{app} is defined by eq 2.

The values of A_3 at 34.5 °C are given in the last column of Table I and are plotted double-logarithmically against M_w in Figure 7, in which our previous A_3 data[1,2] in benzene at 25 °C are also shown. The A_3 values in the Θ solvent are 1 or 2 orders of magnitude smaller than those in the good solvent at any M_w and are relatively insensitive to M_w; we note that the A_3(Θ) data for the two highest molecular weight fractions are less accurate because the measurements were confined to low-concentration regions in which $S(c_1,c_2)$ values are not removed much from zero (see Figure 3).

As mentioned in the Experimental Section, the highest polymer concentration studied for a given polystyrene fraction is 2–4 times higher than that investigated pre-

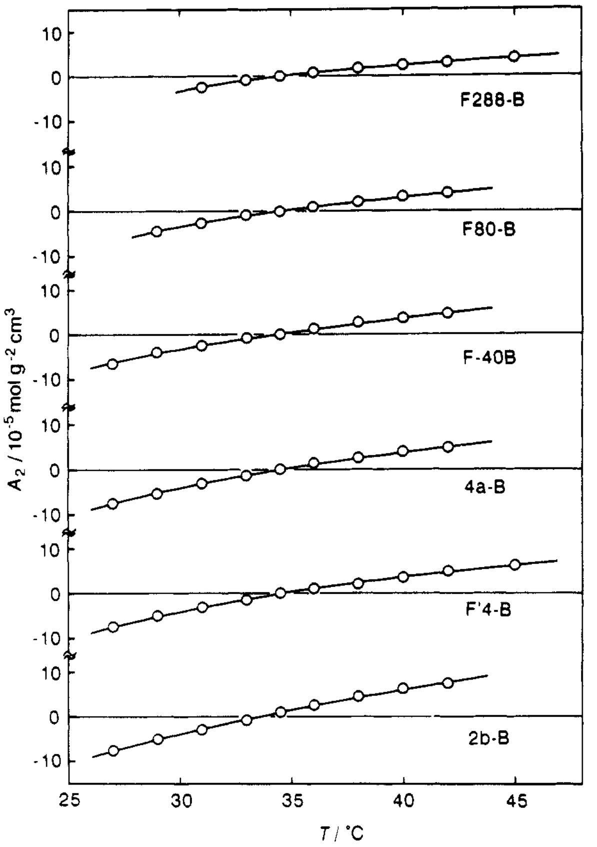

Figure 5. Temperature dependence of A_2 for polystyrene fractions in cyclohexane.

Table I
Results for M_w, A_2, and A_3 for Polystyrene Fractions in Cyclohexane at 34.5 °C

fraction	$10^{-4}M_w$	A_2, mol g^{-2} cm^3	10^4A_3, mol g^{-3} cm^6
2b-B	2.07 1.98[a]	1.0×10^{-5}	$5._4$
F'4-B	5.07	0	$5._0$
4a-B	9.97 9.79[a]	0	$4._3$
F-40B	37.3 37.9[a]	0	$4._2$
F80-B	84.3 84.5[a]	0	7
F288-B	300 315[a]	0[b]	9

[a] In benzene at 25 °C.[1,2] [b] The graphically determined value is 2×10^{-6} mol g^{-2} cm^3.

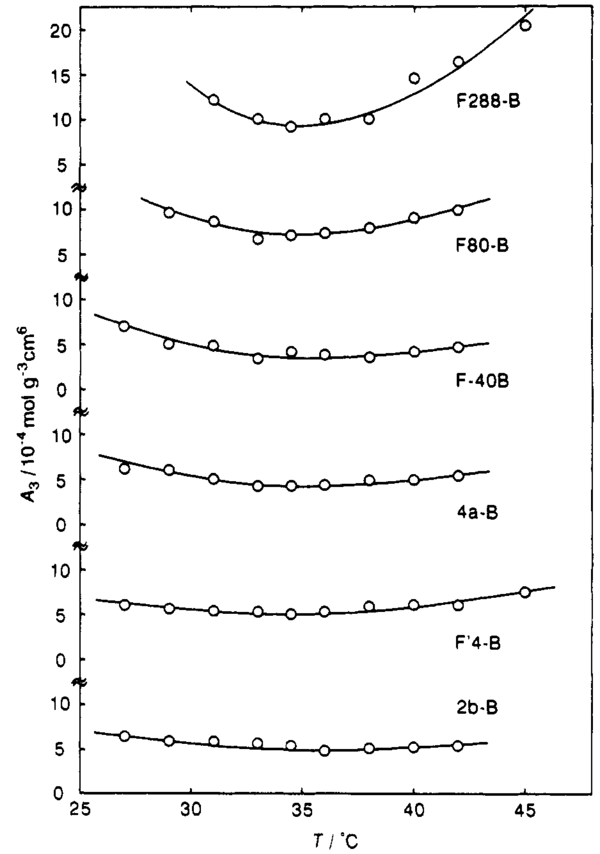

Figure 6. Temperature dependence of A_3 for polystyrene fractions in cyclohexane.

viously[1,2] for benzene solutions. In the previous work, distinct downward curvatures were observed in Bawn plots when the measurement on benzene solutions was extended to such high concentrations. On the other hand, any Bawn plots for cyclohexane solutions in this work show no discernible curvature, suggesting that in poor solvents the second and third virial terms dominate $[(Kc/R_0) - (1/M_w)]$ over a wider concentration range than in good solvents. Since the fourth virial contributions to the $S(c_1,c_2)$ vs $c_1 + c_2$ and $[(Kc/R_0) - (1/M_w)]/c$ vs c relations are different (compare eq 1 with the relation $[(Kc/R_0) - (1/M_w)]/c = 2A_2 + 3A_3c + 4A_4c^2 + ...$), the following data analysis was made to ensure that Kc/R_0 at Θ contains no substantial A_4 contribution in the range of c studied.

When $A_2 = 0$, Kc/R_0 is written as

$$Q \equiv [(Kc/R_0) - (1/M_w)]/c^2$$
$$= 3A_3 + 4A_4c + ... \qquad (A_2 = 0) \qquad (3)$$

which indicates that Q is essentially independent of c if it is dominated by A_3 in the concentration range considered; we note that this equation is applicable when an accurate M_w is known in advance. Figure 8 shows the plots of Q vs c constructed from the Kc/R_0 data in cyclohexane at 34.5 °C and the M_w data in benzene for the three fractions 4a-B, F-40B, and F80-B whose M_w values in the two solvents agreed within ±1% (see Table I). We have omitted intensity data at low c where Kc/R_0 is not removed from the input value of $1/M_w$ by more than 1%. All the plotted points except two at the lowest c for fractions 4a-B and F-40B fall on horizontal lines for the respective fractions, yielding $A_3(\Theta)$ of 4×10^{-4}, 5×10^{-4}, and 7×10^{-4} mol g^{-3} cm^6 for fractions 4a-B, F40-B, and F80-B, respectively; the deviations of the two points from the lines are probably immaterial, since the differences between Kc/R_0 and $1/M_w$ values for them are only about 2%. The substantial agreement of these $A_3(\Theta)$ values with those in Table I, along with the observed c-independent behavior of Q, convinces us that A_4 has a negligible contribution to Kc/R_0 when the Bawn plot is linear.

With the experimental relation $\langle S^2 \rangle_0 = 8.8 \times 10^{-18}M_w$ cm^2 reported by Miyaki et al.[10,11] for polystyrene in cyclohexane at 34.5 °C, the overlap concentration (c^*) defined by $c^* = 3M_w/(4\pi N_A \langle S^2 \rangle_0^{3/2})$ was estimated for each fraction, where N_A is the Avogadro constant and $\langle S^2 \rangle_0$ is the mean-square radius of gyration at the Θ point. The calculated c^* values were 20–30% higher than the highest concentrations studied for the three fractions F'4-B, 4a-B, and F-40B and 2–3 times higher than those for the others. Thus, we find that at least for these three fractions the concentration dependence of $[(Kc/R_0) - (1/M_w)]$ in cyclohexane at 34.5 °C is determined substantially by A_3 only over a wide range of c from 0 to $0.7c^*$.

Nonetheless, there is a low-concentration region in which Kc/R_0 at Θ is practically unaffected by A_3. For example,

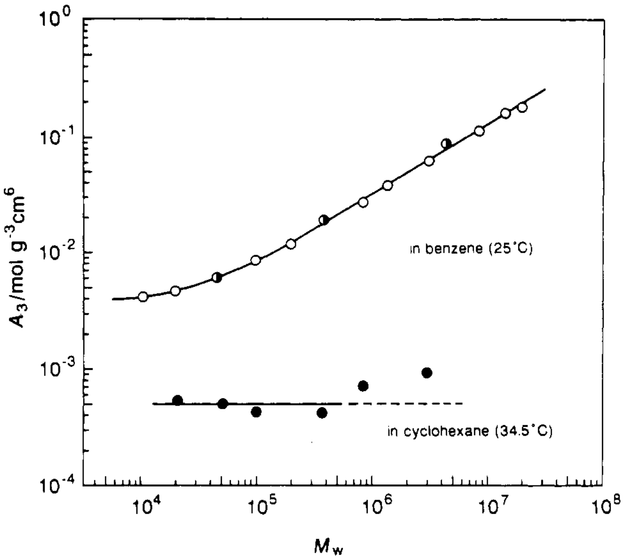

Figure 7. Molecular weight dependence of A_3 for polystyrene in cyclohexane at 34.5 °C (the filled circles) and in benzene at 25 °C (the half-filled circles[1] and the unfilled circles[2]).

Kc/R_0 calculated for fraction 4a-B with the M_w and $A_3(\Theta)$ values in Table I stays equal to $1/M_w$ within 1% up to as high a c as 8.8×10^{-3} g cm^{-3} ($=0.18c^*$). Such c-independent behavior of Kc/R_0 yielding $A_2 = 0$ is just what is usually observed in Θ solvents. In this connection, it should be noticed in Figure 1 that Θ for fraction 4a-B appears to be not at 34.5 °C but at 33 °C owing to the compensation of negative A_2 and positive A_3 (see Figures 5 and 6) in the range of c between 1×10^{-2} and 2×10^{-2} g cm^{-3}. Hence, Θ may be underestimated if light-scattering data at relatively high c are analyzed by the conventional Kc/R_0 vs c plot.

Comparison with Perturbation Theories. Since A_3 for polystyrene in cyclohexane has been found to remain positive at Θ, it seems almost mandatory to take at least three-body segment interactions into consideration in discussing A_3 (and probably A_2 as well) near the Θ point. In the following, we compare the present A_2 and A_3 data at Θ with the first-order perturbation theories[13] formulated for linear flexible chains (Gaussian chains in the unperturbed state) with the ternary cluster integral β_3 incorporated, i.e.,

$$A_2 = \frac{N_A n^2}{2M^2}\left\{\beta_2 + \frac{4}{\sigma^{1/2}}\left(\frac{3}{2\pi b^2}\right)^{3/2}\beta_3\left[1 - 2\left(\frac{\sigma}{n}\right)^{1/2}\right] + \text{orders in } \beta_2{}^2, \beta_2\beta_3, \text{and } \beta_3{}^2\right\} \quad (4)$$

$$A_3 = \frac{N_A{}^2 n^3}{3M^3}(\beta_3 + \text{orders in } \beta_2\beta_3, \beta_3{}^2, \text{and } \beta_2{}^3) \quad (5a)$$

$$A_3 = \frac{N_A{}^2}{3}\left(\frac{4\pi\langle S^2\rangle_0}{M}\right)^3(z_3 + \ldots) \quad (5b)$$

where

$$z_3 = \left(\frac{3}{2\pi b^2}\right)^3\beta_3 \quad (6)$$

In these equations, n is the number of segments (or monomeric units) in one chain, β_2 is the binary cluster integral, b is the segment length, and σ is a certain cut-off parameter that, in the ordinary discrete chain model, may be considered to represent approximately the minimum number of consecutive segments necessary for the formation of a loop within one chain. We note that the $n^{-1/2}$ term in the braces of eq 4 is not affected by the stiffness or non-Gaussian nature of short chains.[15]

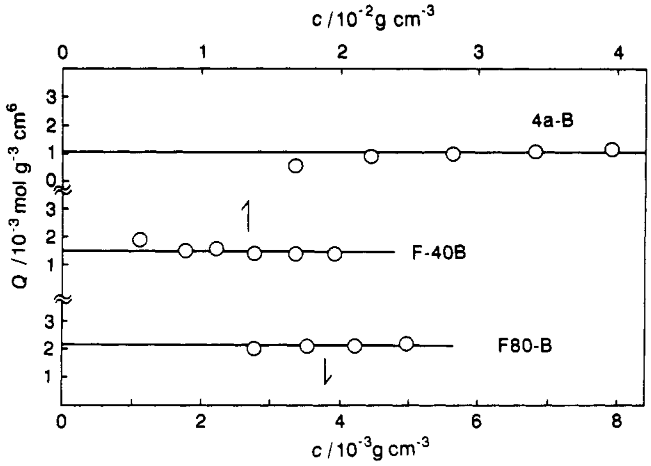

Figure 8. Plots of Q vs c for indicated polystyrene fractions in cyclohexane at the Θ point. Q is defined by eq 3.

Equation 5a or eq 5b predicts that when both β_2 and β_3 are vanishingly small, $A_3(\Theta)$ is independent of M. This is consistent with the behavior of $A_3(\Theta)$ observed for $M_w < 4 \times 10^5$ in Figure 7. If, as was proposed by Cherayil et al.,[14] eq 5a is applied to the $A_3(\Theta)$ data in this molecular weight region, a value of 5×10^{-45} cm^6 is obtained for β_3, which in turn yields 0.003 for z_3 when use is made of the $\langle S^2\rangle_0$–M_w relation of Miyaki et al.[10,11] This z_3 value happens to be close to 0.0045 estimated recently by Chen and Berry[17] from scattering intensity data on moderately concentrated solutions of a polystyrene sample ($M_w = 8.6 \times 10^5$) in cyclohexane at the Θ temperature.

Equation 4 indicates that the Θ state is attained by compensation of negative β_2 and positive $(4/\sigma^{1/2})(3/2\pi b^2)^{3/2}\beta_3$ values regardless of M provided $n^{1/2}$ is much larger than $\sigma^{1/2}$ and both β_2 and β_3 are vanishingly small. However, the $n^{-1/2}$ term in the equation is not always negligible, and Θ should increase with decreasing M since the theoretical $A_2(\Theta_\infty)$ ($=A_2$ at Θ_∞, the Θ point for infinitely long chains) is an increasing function of n for positive β_3. An A_2 value of the order 10^{-6} mol g^{-2} cm^3 is experimentally indistinguishable from zero, so that for the Θ to be practically independent of M, the contribution of the $n^{-1/2}$ term to A_2 has to be less than 5×10^{-6} mol g^{-2} cm^3 at Θ_∞, i.e.,

$$\frac{4N_A n^2}{M^2}\left(\frac{3}{2\pi b^2}\right)^{3/2}\left(\frac{\beta_3}{n^{1/2}}\right) < 5 \times 10^{-6} \text{ mol g}^{-2}\text{ cm}^3$$

Substituting the β_3 value estimated above from A_3, we find that this inequality is satisfied for M above 3×10^6. This molecular weight is almost 2 orders of magnitude larger than the experimental value of 5×10^4 above which Θ is substantially constant. In other words, as M decreases, $A_2(\Theta_\infty)$ in eq 4 begins to decrease appreciably from zero at $M \sim 3 \times 10^6$, in contrast to the experimental fact that A_2 at 34.5 °C stays virtually zero down to $M_w \sim 5 \times 10^4$ and tends to *increase* with a further decrease in M_w. In short, we find no consistent value for β_3 with which eqs 4 and 5 explain the present A_2 and A_3 data at the Θ temperature.

Huber and Stockmayer[12] found that the smoothed-density theory of Orofino and Flory[18] for A_2 containing β_3 (see eq 17 of ref 18) qualitatively explains the above-mentioned increase in experimental A_2 (at 35 °C) and hence the decrease in Θ with decreasing M_w (below 10^4). In this theory, the Θ condition is given by[19] $\beta_2 + 3^{3/2}$-

$(3/2\pi b^2)^{3/2}\beta_3 n^{-1/2} = 0$ and thus Θ_∞ by $\beta_2 = 0$, differing from what is predicted by eq 4; i.e., $\beta_2 + (4/\sigma^{1/2})(3/2\pi b^2)^{3/2}\beta_3 = 0$. If the same β_3 value of 5×10^{-45} cm^6 as estimated above on the basis of the first-order expansion is used, Orofino and Flory's $A_2(\Theta_\infty)$ is found to begin deviating from zero (more correctly from 5×10^{-6} mol g^{-2} cm^3) at $M \sim 10^6$. Thus, with this β_3 value, their theory also fails to explain the molecular weight independent Θ for M_w above 5×10^4.

Conclusions

(1) The third virial coefficient for polystyrene in cyclohexane at Θ where $A_2 = 0$ is 4×10^{-4}–9×10^{-4} mol g^{-3} cm^6 for M_w between 2×10^4 and 3×10^6, and thus, the two-parameter theory for it breaks down at least under the Θ condition.

(2) The Θ temperature for this system is essentially independent of molecular weight if M_w is higher than 5×10^4.

(3) The first-order perturbation theories of A_2 and A_3 for linear flexible chains with three-body segment interactions fail to explain consistently the above A_3 values and the second conclusion.

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(13) See, for example, ref 14. For convenience, both A_2 and A_3 are expressed in terms of the ordinary discrete chain model differing from the continuous chain version in ref 14.

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(15) If Yamakawa and Stockmayer's wormlike bead model[16] is used, along with their theory for the ring-closure probability, A_2 is evaluated to be

$$A_2 = \frac{N_A n^2}{2M^2}\left\{\beta_2 + \beta_3\left(\frac{3}{2\pi(b')^2}\right)^{3/2}\left[3.159 - \frac{8}{n^{1/2}} + O\left(\frac{1}{n}\right)\right] + \ldots\right\}$$

where, for simplicity, Kuhn's segment length has been taken to equal the bead spacing b' along the chain contour; n denotes the number of Kuhn segments. The $n^{-1/2}$ term in the braces of this equation coincides with that in eq 4.

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