

Second and Third Virial Coefficients for Polyisobutylene in the Vicinity of the Theta Point

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ABSTRACT: The second virial coefficient A_2 and the third virial coefficient A_3 have been determined for five polyisobutylene fractions ranging in weight-average molecular weight M_w from 8×10^4 to 1.6×10^6 in isoamyl isovalerate at different temperatures T between 21 and 37°C by light scattering. The theta temperature Θ where A_2 vanishes is found to be 27°C independent of M_w . The curve of A_3 vs. T obtained for each fraction has a broad minimum around Θ , and the minimum becomes very shallow as M_w decreases. These features are very similar to those observed previously for polystyrene in cyclohexane. The values of A_3 at Θ are in the range between 3×10^{-4} and 7×10^{-4} mol g⁻³ cm⁶, and thus demonstrate the breakdown of the binary cluster approximation to A_3 for polyisobutylene near Θ . It is shown that existing theories of A_2 and A_3 are incapable of explaining consistently the positive A_3 at Θ and the molecular weight independence of Θ in the range of M_w studied, as found to be the case for polystyrene.

KEY WORDS Second Virial Coefficient / Third Virial Coefficient / Polyisobutylene / Theta Point / Three-Segment Interaction / Two-Parameter Theory / Light Scattering /

In previous work,¹ we found from light scattering measurements that the third virial coefficient A_3 for polystyrene in cyclohexane remains positive at the theta temperature Θ where the second virial coefficient A_2 equals zero. This reveals the breakdown of the two-parameter theory² for A_3 near the theta point, since the theory predicts that A_2 and A_3 simultaneously vanish at Θ . Another important finding in the previous study was that A_3 increases with a decrease in temperature below Θ . This is also contrasted to the two-parameter theory prediction that A_3 should become negative below Θ .

It is intriguing to see whether the above findings are common to other linear flexible chains in theta solvents. This motivated us to perform similar light scattering measurements on sharp fractions of polyisobutylene (PIB), another typical flexible polymer. Isoamyl isovalerate (IAIV) was chosen as the solvent,

because it brings the polymer to the theta state at room temperature and gives a refractive index increment large enough for light scattering experiment.^{3,4} Data were obtained not only for A_2 and A_3 but also for the z -average mean-square radius of gyration $\langle S^2 \rangle_z$ as functions of molecular weight and temperature. The virial coefficient data at Θ are discussed below in relation to three-segment interactions.

EXPERIMENTAL

Preparation of Solutions

Five PIB fractions with molecular weights of 8×10^4 — 1.6×10^6 (in cyclohexane) were chosen from the previously investigated samples.⁵ The ratios of the weight-average to number-average molecular weight estimated from gel permeation chromatography (GPC) in chloroform were in the range 1.08—1.10.⁵

The solvent IAIV (Tokyo Kasei Kogyo Co.) was washed twice with 2*N* aqueous sodium carbonate and three times with water, dehydrated with anhydrous potassium carbonate, and fractionally distilled twice under reduced nitrogen atmosphere. Each polymer sample was mixed with the solvent in a dry bag filled with nitrogen. The mixture was gently stirred in the dark for 2–10 days at 35°C, with care taken to ensure complete dissolution of the polymer and to prevent it from degradation.

The polymer mass concentration c of each solution was calculated from the polymer weight fraction with the solution density ρ . The density was measured at 20, 30, and 40°C using a bicapillary pycnometer of 30 cm³ capacity. The results for $c \lesssim 3 \times 10^{-2} \text{ g cm}^{-3}$ were found to be represented by

$$\rho = 0.85503 + 0.0714c \quad (20^\circ\text{C})$$

$$\rho = 0.84631 + 0.0761c \quad (30^\circ\text{C})$$

$$\rho = 0.83762 + 0.0806c \quad (40^\circ\text{C})$$

where both c and ρ are expressed in units of g cm⁻³. Necessary values of ρ at different temperatures were obtained by interpolation.

Light Scattering Measurement

Light scattering measurements were carried out at temperatures ranging from 21 to 37°C on a Fica-50 light scattering photometer with vertically polarized incident light of 436 nm wavelength in an angular range from 30 to 150°. Pure benzene at 25°C was used to calibrate the apparatus. Its Rayleigh ratio at 436 nm was taken to be $46.5 \times 10^{-6} \text{ cm}^{-1}$,⁶ and its depolarization ratio was determined to be 0.40 by the method of Rubingh and Yu.⁷ The specific refractive index increment $\partial n/\partial c$ for PIB in IAIV at 436 nm was determined at 25, 30, 35, and 40°C using a modified Schulz–Cantow type differential refractometer, with the result that for $c \lesssim 4.5 \times 10^{-2} \text{ g cm}^{-3}$

$$\partial n/\partial c = 0.1100 - 0.06c \quad (25^\circ\text{C})$$

$$\partial n/\partial c = 0.1113 - 0.08c \quad (30^\circ\text{C})$$

$$\partial n/\partial c = 0.1127 - 0.11c \quad (35^\circ\text{C})$$

$$\partial n/\partial c = 0.1140 - 0.14c \quad (40^\circ\text{C})$$

where $\partial n/\partial c$ is expressed in units of cm³ g⁻¹. Necessary $\partial n/\partial c$ values at different temperatures were obtained by interpolation. The infinite-dilution value of 0.1100 cm³ g⁻¹ at 25°C is in excellent agreement with the values 0.1091 and 0.1103 cm³ g⁻¹ reported by Matsumoto *et al.*³ and by Abe *et al.*,⁴ respectively.

Refractive indices of IAIV were determined by a precision sugar refractometer (Bausch and Lomb Co.) to be 1.421₇ at 20.1°C, 1.417₅ at 29.9°C, and 1.412₈ at 39.9°C for light of the wavelength 436 nm.

RESULTS

Molecular Weight and Virial Coefficients

Scattering intensity data obtained were extrapolated to zero angle using Berry's square-root plot⁸ of $(Kc/R_\theta)^{1/2}$ vs. $\sin^2(\theta/2)$, where K is the optical constant and R_θ the reduced scattering intensity at a scattering angle θ . Figure 1 illustrates the concentration dependence of Kc/R_θ at zero scattering angle, *i.e.*, Kc/R_0 , for PIB fraction S-14B at the indicated temperatures T . The curves fitting the data points at the respective T bend upward and appear to converge to a common ordinate intercept.

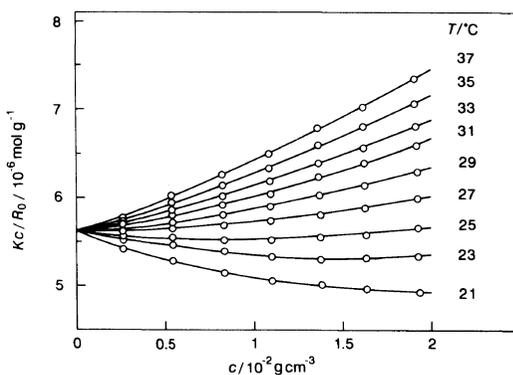


Figure 1. Concentration dependence of scattering intensity at zero angle for PIB fraction S-14B in IAIV at indicated temperatures.

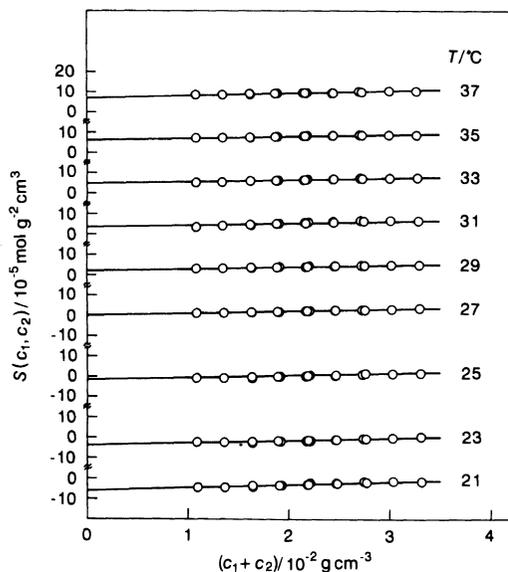


Figure 2. Bawn plots constructed from the data in Figure 1 according to eq 1.

The values of Kc/R_0 at finite concentrations were analyzed using the expression^{9,10} (originally derived by Bawn *et al.*¹¹ for osmotic pressure)

$$S(c_1, c_2) \equiv \frac{(Kc/R_0)_{c=c_2} - (Kc/R_0)_{c=c_1}}{c_2 - c_1} = 2A_2 + 3A_3(c_1 + c_2) + \dots \quad (1)$$

where c_1 and c_2 denote different polymer mass concentrations. The Bawn plots of $S(c_1, c_2)$ vs. $c_1 + c_2$ constructed from the data in Figure 1 are shown in Figure 2. The plotted points at each T follow a straight line, whose intercept and initial slope permit us to determine A_2 and A_3 separately. Similar plots for five PIB fractions at 27.0°C are displayed in Figure 3.

The weight-average molecular weight M_w can be obtained by extrapolation of the apparent molecular weight defined by⁹

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

to infinite dilution. Figure 4 shows the plots of M_{app} vs. c for five fractions at 27.0°C. The plotted points for each fraction fall essentially on a horizontal line, allowing unambiguous

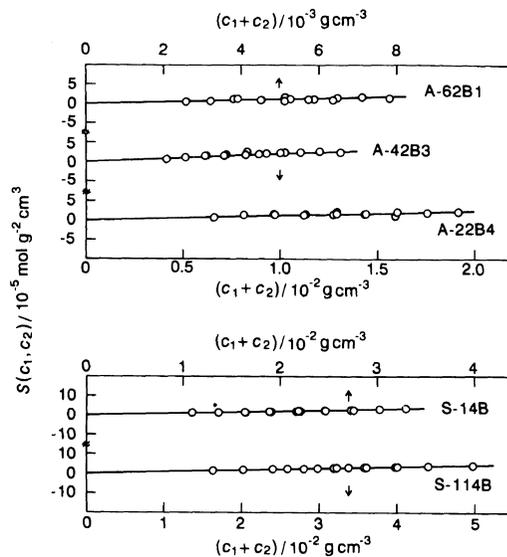


Figure 3. Bawn plots for the indicated PIB fractions in IAIV at 27°C.

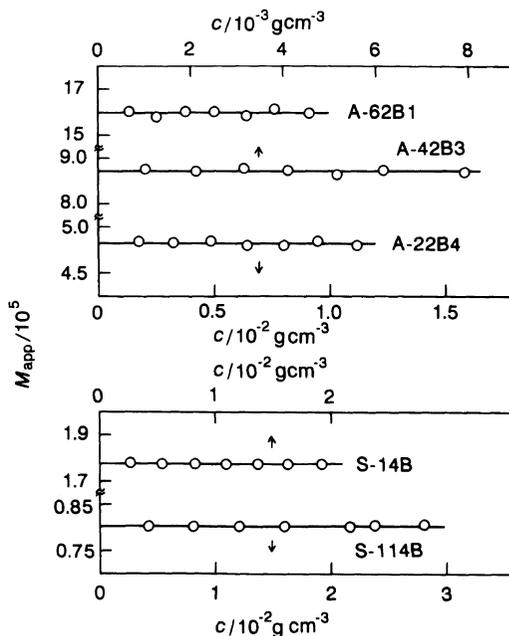


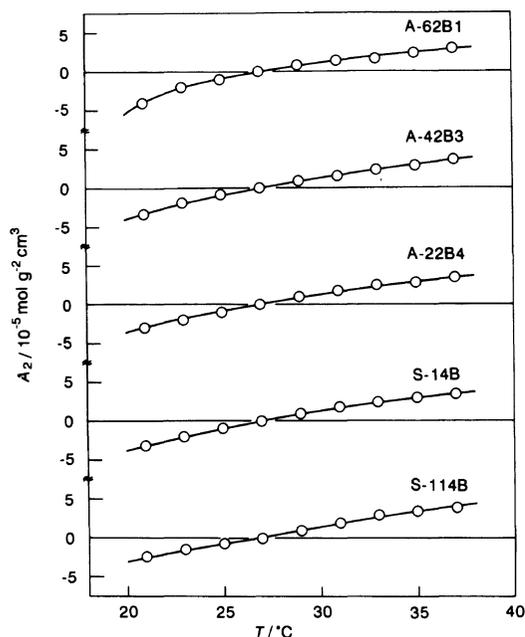
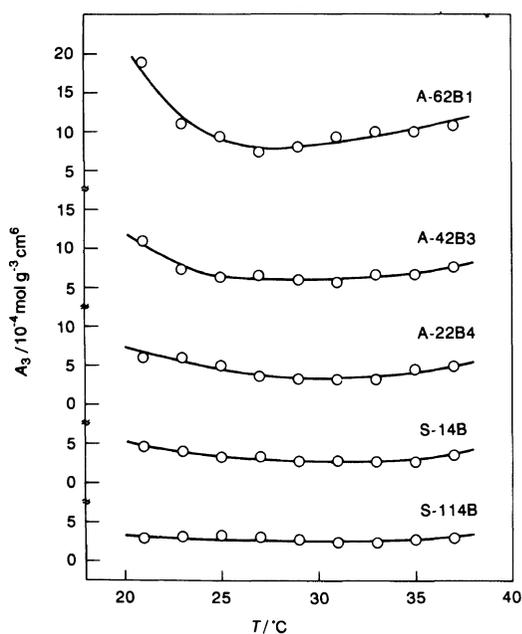
Figure 4. Plots of M_{app} vs. c for the indicated PIB fractions in IAIV at 27°C. M_{app} is defined by eq 2.

determination of M_w . The M_w values determined at different temperatures agreed within $\pm 1.6\%$ for any fractions.

The values of A_2 for five PIB fractions in

Table I. Second virial coefficients for PIB fractions in IAIV at different temperatures

$T/^\circ\text{C}$	$A_2/10^{-5} \text{ mol g}^{-2} \text{ cm}^3$				
	S-114B $M_w = 8.04 \times 10^4$	S-14B $M_w = 17.8 \times 10^4$	A-22B4 $M_w = 48.2 \times 10^4$	A-42B3 $M_w = 87.2 \times 10^4$	A-62B1 $M_w = 160 \times 10^4$
21.0	-2.3	-3.1	-3.0	-3.3	-4.0
23.0	-1.4	-2.0	-2.0	-1.9	-2.0
25.0	-0.6	-0.9	-1.0	-0.8	-1.0
27.0	0.0	0.0	0.0	0.0	0.0
29.0	1.0	1.0	1.0	0.9	0.8
31.0	2.0	1.8	1.8	1.5	1.3
33.0	3.0	2.5	2.5	2.3	1.9
35.0	3.5	3.0	2.8	2.8	2.4
37.0	4.0	3.5	3.5	3.3	3.0

**Figure 5.** Temperature dependence of A_2 for the indicated PIB fractions in IAIV.**Figure 6.** Temperature dependence of A_3 for the indicated PIB fractions in IAIV.

IAIV at different temperatures are summarized in Table I, together with those of M_w at 27°C , and plotted against T in Figure 5. The theta temperature where $A_2=0$ is determined as $27.0 \pm 0.05^\circ\text{C}$ independent of M_w in the molecular weight region studied. The molecular-weight independence of Θ is consistent with the findings by Matsumoto *et al.*³ ($1.6 \times 10^5 <$

$M_w < 4.7 \times 10^6$) and by Abe *et al.*⁴ ($4.2 \times 10^5 < M_w < 1.2 \times 10^6$). However, our Θ value is higher by about 2–5°C than those determined by these previous workers. This discrepancy in Θ among the three groups may be due to some subtle difference in the purity of the IAIV used.

The temperature dependence of A_3 is shown

Table II. Third virial coefficients for PIB fractions in IAIV at different temperatures

$T/^\circ\text{C}$	$A_3/10^{-4} \text{ mol g}^{-3} \text{ cm}^6$				
	S-114B $M_w = 8.04 \times 10^4$	S-14B $M_w = 17.8 \times 10^4$	A-22B4 $M_w = 48.2 \times 10^4$	A-42B3 $M_w = 87.2 \times 10^4$	A-62B1 $M_w = 160 \times 10^4$
21.0	3.0	4.7	6.0	11	19
23.0	3.2	4.0	6.0	7.3	11
25.0	3.3	3.3	5.0	6.3	9.3
27.0	3.1	3.3	3.7	6.7	7.3
29.0	2.8	2.8	3.3	6.0	8.0
31.0	2.5	2.8	3.3	5.7	9.3
33.0	2.5	2.8	3.3	6.7	10
35.0	2.9	2.8	4.7	6.7	10
37.0	3.1	3.7	5.0	7.7	11

in Figure 6. The curve for each fraction has a broad, positive minimum around the theta temperature 27°C and the minimum becomes very shallow as M_w decreases. These features are quite similar to what was observed previously for polystyrene in cyclohexane.¹ The positive A_3 at Θ and its increase with a decrease in T below Θ demonstrate that the two-parameter theory does not hold for PIB in IAIV; we note again that the theory predicts A_3 to vanish at Θ and to be negative below Θ . The numerical data for A_3 are presented in Table II.

In previous work,¹ we showed that $A_3(\Theta)$, the value of A_3 at the theta temperature, can also be estimated from the intercept of a plot of Q vs. c based on the relation

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

where A_4 denotes the fourth virial coefficient. This method has an advantage that A_3 is estimated separately from A_4 even when Kc/R_0 contains some contribution from A_4 in the concentration range examined, though for its practical application, a very accurate value of M_w must be known from a separate experiment. The present M_w values for fractions A-22B4, A-42B3, and A-62B1 agreed with those⁵ determined in cyclohexane (a good

solvent) within 1.3%. Thus, with the M_w values in cyclohexane, we constructed plots of Q vs. c for the three fractions in IAIV at 27°C ; we omitted intensity data at low c where the difference between Kc/R_0 and the input value of $1/M_w$ was less than 1%. The plots were essentially horizontal and gave $A_3(\Theta)$ of 5×10^{-4} , 7×10^{-4} , and $6 \times 10^{-4} \text{ mol g}^{-3} \text{ cm}^6$ for fractions A-22B4, A-42B3, and A-62B1, respectively. This c -independent behavior of Q and the substantial agreement of these values with those in Table II lend support to our previous conviction^{1,12} that A_4 has a negligible contribution to Kc/R_0 when the Bawn plot is linear.

As can be seen from Figure 6 or Table II, the values of $A_3(\Theta)$ for PIB in IAIV are relatively insensitive to M_w , being $(5 \pm 2) \times 10^{-4} \text{ mol g}^{-3} \text{ cm}^6$. Murakami *et al.*¹³ estimated $A_3(\Theta)$ for PIB in benzene to be $3 \times 10^{-4} \text{ mol g}^{-3} \text{ cm}^6$ from the osmotic pressure data of Flory and Daoust.¹⁴ This value happens to be close to our $A_3(\Theta)$. We note that these values are one or two orders of magnitude smaller than those in the good solvent cyclohexane.⁵

Chain Dimensions

Since our light scattering measurements were made at concentrations considerably higher than those usually employed in dilute-solution work, no conventional procedure

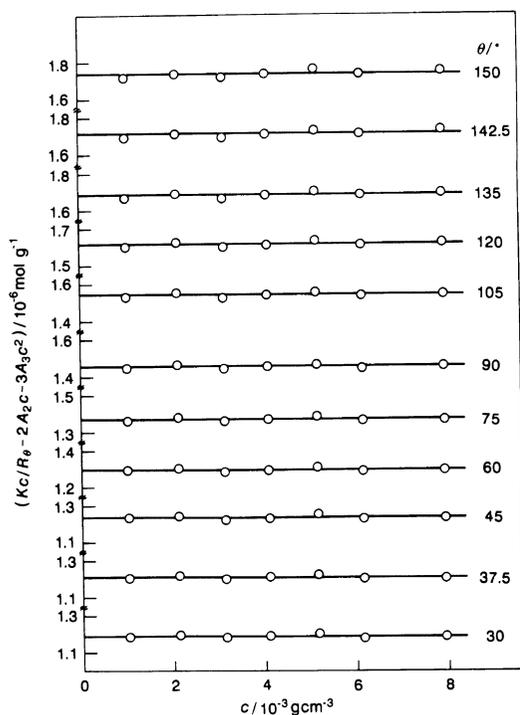


Figure 7. Concentration dependence of $(Kc/R_\theta - 2A_2c - 3A_3c^2)$ for PIB fraction A-42B3 in IAIV at 27°C and fixed scattering angles.

allowed Kc/R_θ at fixed θ to be accurately extrapolated to infinite dilution. When the values of $(Kc/R_\theta - 2A_2c - 3A_3c^2)$ calculated for fixed θ were plotted against c , it was found that the resulting plots for respective θ were essentially horizontal at any T studied and thus gave desired values of $(Kc/R_\theta)_{c=0}$ with high accuracy. Figure 7 illustrates such plots for fraction A-42B3 at 27°C, and the values of $(Kc/R_\theta)_{c=0}^{1/2}$ obtained are plotted against $\sin^2(\theta/2)$ in Figure 8, along with those for other fractions S-14B, A-22B4, and A-62B1 at 27°C. The plotted points for each fraction follow a straight line throughout the entire range of θ examined.

The values of $\langle S^2 \rangle_z^{1/2}$ evaluated are plotted against T in Figure 9, and those at the theta temperature (27°C), *i.e.*, the $\langle S^2 \rangle_{0z}^{1/2}$ values, are presented in Table III, in which the M_w data are the reproductions from Table I. The

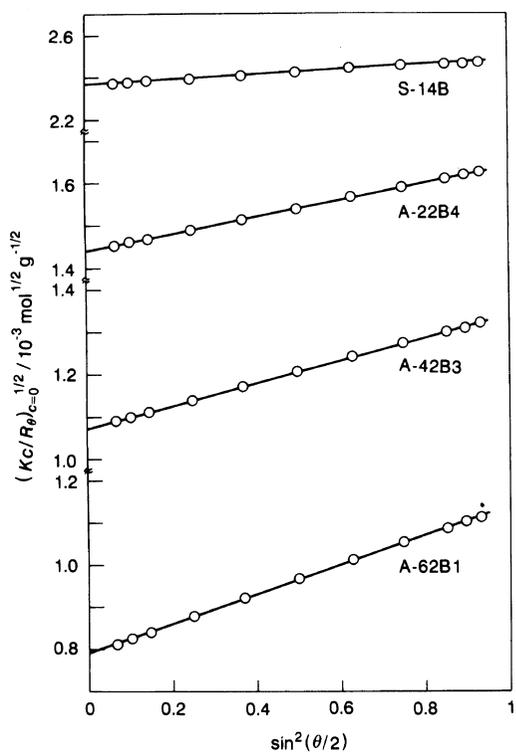


Figure 8. Plots of $(Kc/R_\theta)_{c=0}^{1/2}$ vs. $\sin^2(\theta/2)$ for the indicated PIB fractions in IAIV at 27°C.

Table III. Values of M_w , $\langle S^2 \rangle_{0z}^{1/2}$, and $[\eta]_0$ for PIB fractions in IAIV at the theta temperature

Fraction	$M_w/10^4$	$\langle S^2 \rangle_{0z}^{1/2}$	$[\eta]_0$
		nm	$10^2 \text{ cm}^3 \text{ g}^{-1}$
S-114B	8.04	—	0.304
S-14B	17.8	13.2	0.472
A-22B4	48.2	22.1	0.780
A-42B3	87.2	29.7	1.05
A-62B1	160	39.7	1.42

ratio of $\langle S^2 \rangle_{0z}$ to M_w at 27°C is $(1.00 \pm 0.02) \times 10^{-17} \text{ cm}^2$ independent of M_w , being consistent with the above finding from A_2 that the theta temperature is 27°C for PIB in IAIV. The value $1.00 \times 10^{-17} \text{ cm}^2$ for the unperturbed dimensions $\langle S^2 \rangle_{0z}/M_w$ agrees closely with the reported data ($9.52 \times 10^{-18} \text{ cm}^2$ by Matsumoto *et al.*³ and $9.83 \times 10^{-18} \text{ cm}^2$ by

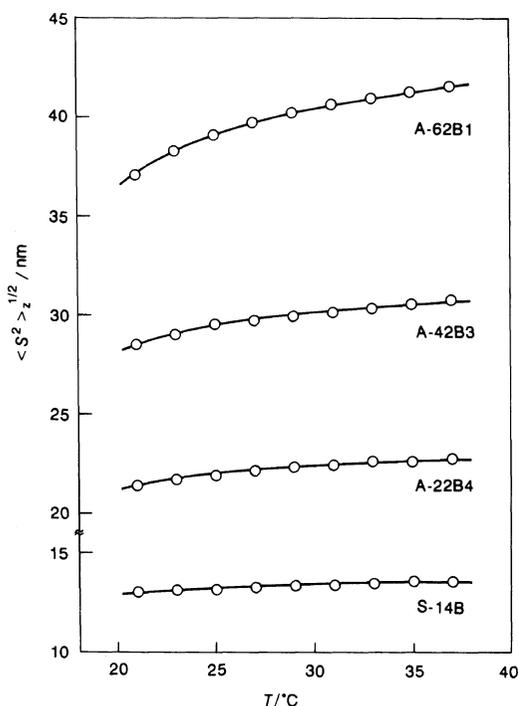


Figure 9. Temperature dependence of $\langle S^2 \rangle_z^{1/2}$ for the indicated PIB fractions in IAIV.

Konishi *et al.*¹⁵) despite the fact that the theta temperatures are at variance.

We also determined intrinsic viscosities $[\eta]_0$ for five PIB fractions in IAIV at 27°C to ascertain that the theta temperature of 27°C is consistent with $[\eta]_0$. This is substantiated by the $[\eta]$ data presented in Table III, from which it can be shown that $[\eta]_0$ is accurately proportional to $M_w^{1/2}$. The proportionality constant $[\eta]_0/M_w^{1/2}$ is $0.112 \text{ cm}^3 \text{ g}^{-1}$. This value is again in excellent agreement with the published data ($0.114 \text{ cm}^3 \text{ g}^{-1}$ by Matsumoto *et al.*³ and $0.109 \text{ cm}^3 \text{ g}^{-1}$ by Abe *et al.*⁴ for $M_w > 2 \times 10^4$). In passing, our $\langle S^2 \rangle_{0z}$ and $[\eta]_0$ data yield on the average $2.4 \times 10^{23} \text{ mol}^{-1}$ for the Flory viscosity factor Φ_θ . If correction is made for polydispersity with the M_z/M_w ratio of 1.09 (M_z is the z -average molecular weight) from our previous GPC data⁵ on the assumption that the GPC curve represents the molecular weight distribution, then Φ_θ for

“monodisperse” PIB is obtained as $2.7 \times 10^{23} \text{ mol}^{-1}$, a value very close to that reported by Konishi *et al.*¹⁵

DISCUSSION

Third Virial Coefficient

We have found that A_3 of PIB in IAIV remains positive at the theta temperature as is the case for polystyrene in cyclohexane.¹ This implies that the binary cluster approximation is no longer valid for A_3 of these typical flexible polymers near the theta point. If the ternary cluster integral β_3 representing the interaction among three segments is incorporated into theory, A_3 near Θ is expressed by^{16,17}

$$A_3 = \frac{N_A^2 n^3}{3M^3} [\beta_3 + O(\beta_2\beta_3, \beta_3^2, \beta_2^3)] \quad (4)$$

or

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

where

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

In these equations, N_A is the Avogadro constant, n the number of segments in one chain, β_2 the binary cluster integral, and b the segment length.

Equation 4 indicates that $A_3(\Theta)$ is insensitive to M if both β_2 and β_3 are vanishingly small. This appears to be consistent with our $A_3(\Theta)$ data. Substituting $A_3(\Theta) = (5 \pm 2) \times 10^{-4} \text{ mol g}^{-3} \text{ cm}^6$ into eq 4 truncated at the leading term, we obtain $(7 \pm 3) \times 10^{-46} \text{ cm}^6$ for β_3 , which yields $z_3 = 0.002 \pm 0.001$ when use is made of $b = 0.58 \text{ nm}$ derived from our relation $\langle S^2 \rangle_{0z}/M_w = 1.00 \times 10^{-17} \text{ cm}^2$. This z_3 value is much smaller than unity, but, as discussed below, the ternary cluster interaction brings about a serious problem concerning the theta point.

Second Virial Coefficient

If both β_2 and β_3 are taken into account to first order, it can be shown that A_2 for the Gaussian bead model is given by (see also refs 17 and 18)

$$A_2 = \frac{N_A n^2}{2M^2} \times \left\{ \beta_e - 8 \left(\frac{3}{2\pi b^2} \right)^{3/2} \frac{\beta_3}{\sqrt{n}} + O(n^{-1}) \right\} \quad (7)$$

where β_e is the effective binary cluster integral defined by

$$\beta_e = \beta_2 + C\beta_3 \quad (8)$$

with

$$C = 2\zeta \left(\frac{3}{2} \right) \left(\frac{3}{2\pi b^2} \right)^{3/2} \quad (9)$$

In eq 9, $\zeta(x)$ is the Riemann zeta function of variable x ; and $\zeta(3/2) (= 2.612)$ comes from

$$n^{-1} \sum_{i=1}^n (n-i)i^{-3/2} = \zeta \left(\frac{3}{2} \right) - 4n^{-1/2} + O(n^{-1})$$

for large n (see ref 18 for the formulation of the ternary cluster term in A_2). Replacement of the sum by an integral with a cutoff parameter σ gives $C = 4\sigma^{-1/2}(3/2\pi b^2)^{3/2}$ but does not alter the second term in eq 7.¹ This term is not affected by chain stiffness either if the chain is sufficiently long so that its $\langle S^2 \rangle_0$ is proportional to n . With regard to effects of chain stiffness on A_2 near Θ , the following remarks may be in order.

The Kratky–Porod wormlike chain¹⁹ mimics the PIB chain in the unperturbed state.⁴ When use is made of Yamakawa and Stockmayer's ring closure probability²⁰ for the wormlike chain bead model, C and the second term in eq 7 are replaced by $3.159(\lambda b')^2(3/2\pi b'^2)^{3/2}$ and $-8(\lambda b')^{3/2}(3/2\pi b'^2)^{3/2}\beta_3/n^{1/2}$, respectively (in our previous paper,¹ $\lambda b'$ is set equal to unity). Here, b' is the bead spacing to be evaluated from $b' = M_0/M_L$ with M_0 and M_L being the molar mass of a monomer and the molar mass per unit contour length, respectively; the total

contour length of the chain equals nb' . Because of the presence of λ^2 , C for the wormlike chain (or more generally for the helical wormlike chain)²¹ is much smaller than that (eq 9) for the Gaussian model. On the other hand, the second term in eq 7 remains the same for long wormlike chains¹ whose $\langle S^2 \rangle_0$ is proportional to n , since $b'\lambda^{-1}$ can be replaced by b^2 in this case. Thus, eq 7 (truncated at the second term) for the Gaussian model appears to hold for flexible chains provided that C is replaced by an appropriate expression depending on the chain model relevant to the actual polymer considered.

Equation 7 indicates that A_2 for sufficiently long chains vanishes when $\beta_e = 0$. Thus, Θ_∞ , the theta point for infinite n , is the temperature at which a negative β_2 is compensated by a positive $C\beta_3$. As the molecular weight decreases, the second term in eq 7 may become significant. If the β_3 value of $(7 \pm 3) \times 10^{-46} \text{ cm}^6$ estimated above is used together with $b = 0.58 \text{ nm}$, A_2 at Θ_∞ is found to fall below $-5 \times 10^{-6} \text{ mol g}^{-2} \text{ cm}^3$ at an M of the order of 10^6 where effects of chain ends²² are insignificant. This behavior of theoretical A_2 disagrees with our experimental finding that $|A_2|$ for PIB in IAIV at 27°C is less than $5 \times 10^{-6} \text{ mol g}^{-2} \text{ cm}^3$ (*i.e.*, virtually zero) down to $M_w = 8 \times 10^4$. Thus, the current theories of the polymer virial coefficients fail to give a consistent explanation of the measured A_2 and A_3 at Θ . This is not specific to the present polymer + solvent system, since a similar inconsistency between theory and experiment was observed for polystyrene in cyclohexane.¹ In sum, the molecular interpretation of the theta condition in terms of segment interactions still leaves much to be desired. It is one of the most basic problems in polymer physics.

CONCLUSIONS

The third virial coefficient for polyisobutylene in isoamyl isovalerate remains positive at the theta temperature and increases with

decreasing temperature below Θ . These features are very similar to what was found previously for polystyrene in cyclohexane, demonstrating that the binary cluster approximation to A_3 near Θ breaks down for these two typical flexible polymers in the theta solvents. Another important conclusion is that the current theories of the polymer virial coefficients are incapable of explaining the theta condition in terms of segment interactions.

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