Second and Third Virial Coefficients for Polyisobutylene in Heptane, an Intermediate Solvent

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ABSTRACT: Light scattering measurements have been made on nine polyisobutylene (PIB) fractions in heptane, an intermediate solvent, at 25°C to determine the second virial coefficient A_2 and the third virial coefficient A_3 as functions of weight-average molecular weight M_w ranging from 2.7×10^4 to 7.8×10^6 . For six of the fractions, z-average mean-square radii of gyration have also been determined. In the molecular weight range studied, A_2 and A_3 vary as $M_w^{-0.21}$ and $M_w^{0.58}$, respectively, and the factor g defined by $A_3/A_2^2 M_w$ is about 0.33 almost independent of molecular weight. The data of g and Ψ (the interpenetration function) as functions of the cube of the radius expansion factor α_s , combined with previous data in cyclohexane, a good solvent, show that the two-parameter theory breaks down unless α_s^3 is larger than about 2 for g and about 5 for Ψ . It is concluded from the comparison of these g data with the recent theory of Norisuye *et al.* that the failure of the two-parameter theory for g at small α_s^3 is due primarily to the neglect of three-segment interactions and that the effect of chain stiffness on g in heptane is of minor importance in the M_w range studied. On the other hand, the stiffness effect on Ψ for PIB is found to be remarkable even at large α_s^3 . In fact, the different dependences of Ψ on α_s^3 observed for heptane and cyclohexane solutions are explained semiquantitatively by the Yamakawa theory which takes account of the stiffness effect within the binary cluster approximation.

KEY WORDS Second Virial Coefficient / Third Virial Coefficient / Polyisobutylene / Excluded-Volume Effect / Expansion Factor / Three-Segment Interaction / Light Scattering /

Recently, we investigated the third virial coefficient A_3 for polystyrene^{1,2} and polyisobutylene (PIB)^{3,4} in both good and theta solvents by light scattering, and drew the following conclusions from experimental findings together with some theoretical calculations.^{5,6} (1) The effect of three-segment interactions on A_3 is remarkable at and near the theta point Θ at which the second virial coefficient A_2 for high molecular weight M vanishes, so that the binary cluster approximation to A_3 or the two-parameter theory for it at and near Θ completely breaks down. (2) In good solvents, the ternary cluster effect on the reduced third virial coefficient g is appreciable only for relatively low M , and thus the binary

cluster approximation holds for g unless the radius expansion factor $\alpha_s (\equiv \langle S^2 \rangle^{1/2} / \langle S^2 \rangle_0^{1/2})$ is close to unity. Here, g is defined by

$$g = A_3 / A_2^2 M \quad (1)$$

and $\langle S^2 \rangle$ and $\langle S^2 \rangle_0$ are the perturbed and unperturbed mean-square radii of gyration, respectively. (3) The effect of chain stiffness on g in good solvents is rather small differing from the case of A_2 ,^{7,8} though it affects the relation between g and α_s^3 for small α_s^3 owing to the stiffness effect on α_s .^{9–11}

For a deeper understanding of the ternary cluster effect on A_3 we deemed it significant to explore the behavior of g in a solvent intermediate between good and theta solvents,

and undertook a light scattering study, with PIB in heptane at 25°C chosen as the system. According to Matsumoto *et al.*,¹² heptane is such a solvent for PIB. In the work reported below, we present experimental results for A_2 , A_3 , and $\langle S^2 \rangle_z$ (the z -average mean-square radius of gyration) as functions of M_w (the weight-average molecular weight) and compare the g data with our previous data³ for the same polymer in cyclohexane, a good solvent, and also with theoretical predictions. Brief discussions on α_s and the interpenetration function appearing in A_2 are given in relation to the stiffness effect within the binary cluster approximation. We note that three-segment interactions need not be considered explicitly for these properties.^{6,13}

EXPERIMENTAL

Nine PIB fractions ranging in M_w from 2.7×10^4 to 7.8×10^6 were chosen from the previously investigated samples.^{3,4} The weight-average to number-average molecular weight ratios of five of them were 1.08–1.10.³ Each of the chosen fractions (originally vacuum-dried or freeze-dried) was further dried *in vacuo* for more than one day just before use. Its mixture with heptane was stirred gently, especially for high molecular weight fractions ($M_w > 3 \times 10^6$), at room temperature for two to ten days to ensure complete dissolution. The solvent heptane was fractionally distilled over sodium after being refluxed for about 5 h.

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 25°C by a bicapillary pycnometer of 30 cm³ capacity. The results for $c \lesssim 4 \times 10^{-2}$ g cm⁻³ was found to be represented by

$$\rho = 0.67961 + 0.273c + 0.11c^2 \quad (\text{g cm}^{-3})$$

Light scattering intensities were measured at 25°C on a Fica-50 light-scattering photometer in an angular range from 18° to 150° with

vertically polarized incident beam of 436 nm or 546 nm wavelength. The apparatus was calibrated with benzene at 25°C (see ref 14). The depolarization ratio of benzene, determined by the method of Rubingh and Yu,¹⁵ was 0.40 for both 436 nm and 546 nm.

As in our previous work,^{1–4} seven different concentrations were studied for each polymer fraction. They were made optically clean by the method described elsewhere.¹⁴

The specific refractive index increment $\partial n/\partial c$ for PIB in heptane at 25°C was determined by using a modified Schulz-Cantow type differential refractometer. The values obtained were 0.144₄ cm³ g⁻¹ and 0.141₄ cm³ g⁻¹ for 436 nm and 546 nm, respectively, independent of c below 4×10^{-2} g cm⁻³. The value for 436 nm agreed closely with the literature data of Matsumoto *et al.*¹² (0.1422 cm³ g⁻¹) and Abe *et al.*¹⁶ (0.1435 cm³ g⁻¹).

RESULTS

Data Analysis

Figure 1 illustrates the angular dependence of $(Kc/R_\theta)^{1/2}$ for a PIB fraction (S-14B) in heptane at 25°C. Here, K is the optical constant and R_θ is the reduced scattering intensity at a scattering angle θ . The intercept of each line gives the zero-scattering angle value $(Kc/R_0)^{1/2}$.

From the values for Kc/R_0 obtained, a plot

Figure 1. Angular dependence of scattering intensity at the indicated concentrations for PIB fraction S-14B in heptane at 25°C.

Figure 2. Plots of $S(c_1, c_2)$ vs. $c_1 + c_2$ for PIB fractions in heptane at 25°C. $S(c_1, c_2)$ data for pairs of neighboring c_1 and c_2 in a series of polymer concentrations are omitted, since they were not very accurate.

of $S(c_1, c_2)$ vs. $c_1 + c_2$ (referred to as the Bawn plot¹⁷) was constructed according to the equation¹⁸

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

where c_1 and c_2 denote different concentrations. The resulting Bawn plot is shown in Figure 2, along with those constructed for other fractions. The data points for each fraction are fitted by a straight line, whose intercept and slope give $2A_2$ and $3A_3$, respectively.

The molecular weights of all the fractions were determined as follows.¹⁸ The apparent molecular weight defined by

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

was calculated for each fraction with the estimated A_2 and A_3 values and plotted against c . As Figure 3 shows, the plotted points for any fractions fall on the respective horizontal

Table I. Results from light scattering measurements on PIB fractions in heptane at 25°C

Fraction	$M_w \times 10^{-5}$	$A_2 \times 10^4$ mol g ⁻² cm ³	$A_3 \times 10^2$ mol g ⁻³ cm ⁶	$\langle S^2 \rangle_z^{1/2}$ nm
S-111B	0.271	4.96	0.22	—
S-112B	0.425	4.45	0.28	—
S-114B	0.813	3.94	0.40	—
S-14B	1.79	3.22	0.62	15.4
A-22B4	4.87	2.65	1.21	27.9
A-42B3	8.90	2.42	1.73	39.7
A-62B1	15.8	2.08	2.3	55.9
P-32	33.1	1.78	3.4	87.1
P-53	77.5	1.51	6.1	145

lines. The intercepts give the desired M_w .

The z -average mean-square radius of gyration was determined by the usual method.¹⁹ The results for M_w , A_2 , A_3 , and $\langle S^2 \rangle_z$ are all summarized in Table I. The M_w values for five fractions (S-114B, S-14B, A-22B4, A-42B3, A-62B1) agree with the previously determined

Figure 3. Plots of M_{app} vs. c for PIB fractions in heptane at 25°C. M_{app} is defined by eq 3.

values⁴ in isoamyl isovalerate at the theta temperature (27°C) within $\pm 1\%$ and those for six fractions (S-112B, S-14B, A-22B4, A-42B3, A-62B1, P-53), with the previous values³ in cyclohexane within $\pm 1\%$.

Second and Third Virial Coefficients

Figure 4 shows the molecular weight dependence of A_2 for PIB in heptane. It includes the data of Matsumoto *et al.*¹² in the same solvent and those of Nakamura *et al.*³ in cyclohexane (CH), all at 25°C. The agreement between our data and those of Matsumoto *et al.* is very good. The straight lines fitting these two data sets has a slope of -0.21 , whose absolute value is slightly smaller than that (-0.24) for CH solutions.

The molecular weight dependence of A_3 for heptane solutions is shown in Figure 5, along

Figure 4. Molecular weight dependence of A_2 for PIB in heptane at 25°C (circles, this work; triangles, Matsumoto *et al.*¹²) and in CH at 25°C (squares, Nakamura *et al.*³).

Figure 5. Molecular weight dependence of A_3 for PIB in heptane at 25°C (circles, this work) and in CH (squares, Nakamura *et al.*³), both at 25°C.

with that determined previously³ for CH solutions. The A_3 values in heptane are considerably smaller than those in CH, but the slope 0.58 of the indicated straight line for the former solvent is very close to that (0.60) for the latter solvent.

In Figure 6, the values for the reduced third virial coefficient (defined by eq 1) in heptane are compared with those in CH. Interestingly, the g values in the former are about 0.33, regardless of molecular weight, differing from g in the latter which slightly decreases and then increases to about 0.5 with increasing M_w . The two-parameter theory²⁰ predicts that A_2 and A_3 in the good solvent limit vary as $M_w^{-0.20}$

Figure 6. Molecular weight dependence of g for PIB in heptane (circles, this work) and in CH (squares, Nakamura *et al.*³), both at 25°C.

and $M_w^{0.60}$, respectively. The experimental exponents of -0.21 and 0.58 for A_2 and A_3 in heptane happen to be close to these theoretical exponents and indeed lead to M_w -independent g . On the other hand, the increase in g for CH solutions at high M_w is due primarily to the M_w -dependence of A_2 stronger than the two-parameter theory prediction, as discussed previously;^{3,21} note that the same is true for polystyrene in benzene.^{1,14} Since heptane is not as good a solvent for PIB as CH, the observed M_w -independent g for it should not be taken as the asymptotic behavior for flexible chains in good solvents. Another point to note in Figure 6 is that the g values in heptane for $M_w \lesssim 5 \times 10^5$ are comparable to or somewhat larger than those in CH at the same M_w . This contradicts the two-parameter theory prediction that g for a given polymer in an intermediate solvent is always smaller than that in a good solvent at the same molecular weight.

Radius of Gyration

The present $\langle S^2 \rangle_z$ data in heptane (the unfilled circles) are compared with those of Matsumoto *et al.*¹² (the triangles) and Abe *et al.*¹⁶ (the inverted triangles) in Figure 7, in which our previous data in CH (the squares)³ and in isoamyl isovalerate (IAIV)⁴ at the theta temperature (the filled circles) are included. Here, one filled circle ($M_w = 3.32 \times 10^6$, $\langle S^2 \rangle_{0z} = 3.40 \times 10^3 \text{ nm}^2$) is the data obtained for fraction P-32 in this work. The literature data in CH

Figure 7. Molecular weight dependence of $\langle S^2 \rangle_z$ for PIB in heptane at 25°C (unfilled circles, this work; triangles, Matsumoto *et al.*¹²; inverted triangles, Abe *et al.*¹⁶), in CH at 25°C (squares, Nakamura *et al.*³), and in IAIV at the theta temperature 27°C (filled circles, Akasaka *et al.*⁴).

and in IAIV at the theta point by other workers^{12,16} are not shown here, since they were compared with ours previously.^{3,4} All the data points in heptane are seen to be fitted by a single straight line. This line has a slope of 1.18, which does not differ from the value 1.19 in CH.

DISCUSSION

Expansion Factor and Interpenetration Function

For convenience of our discussion, we first examine the behavior of α_s^2 in heptane and CH, with the unperturbed PIB chain modeled by the wormlike bead chain, a special case of the helical wormlike chain.²² In the Yamakawa–Stockmayer–Shimada (YSS) theoretical scheme,^{9–11} α_s is a universal function of the scaled excluded-volume parameter $\tilde{z}$ defined by

$$\tilde{z} = \frac{3}{4} K(\lambda L) z_2 \quad (4)$$

with

$$z_2 = \left(\frac{3}{2\pi}\right)^{3/2} B_2 (\lambda L)^{1/2} \quad (5)$$

and

$$\begin{aligned} K(\lambda L) &= \frac{4}{3} - 2.711(\lambda L)^{-1/2} + \frac{7}{6}(\lambda L)^{-1} \\ &\quad \text{for } \lambda L > 6 \\ &= (\lambda L)^{-1/2} \exp[-6.611(\lambda L)^{-1} \\ &\quad + 0.9198 + 0.03516(\lambda L)] \quad \text{for } \lambda L \leq 6 \end{aligned} \quad (6)$$

In these equations, L is the contour length of the chain, λ^{-1} is the stiffness parameter (equal to the Kuhn segment length in the wormlike chain limit), and B_2 is defined by $B_2 = \beta_2 \lambda / l^2$ with β_2 the binary cluster integral and l the bead spacing; in the coil limit, $\tilde{z}$ becomes equal to the excluded-volume parameter in the two-parameter theory.²⁰ The effect of chain stiffness on α_s for a given polymer comes from the deviation of $K(\lambda L)$ from the coil-limiting value of 4/3. As mentioned in the Introduction, the ternary cluster effect, if any, is absorbed in the binary cluster term and hence does not need to be considered as far as α_s and A_2 are concerned.^{6,13}

Assuming that the shift factor $M_L (= M/L)$ of the PIB chain is equal to 241 nm^{-1} ,¹⁶ we obtain $\lambda^{-1} = 1.4 \text{ nm}$ from the $\langle S^2 \rangle_{0z}$ data in Figure 7 and the relation $\langle S^2 \rangle_0 = M / (6\lambda M_L)$ for long wormlike chains. If these wormlike chain parameters are applied to heptane and CH solutions, B_2 is estimated to be 0.08 in heptane and 0.22 in CH from the slopes of $\langle S^2 \rangle_z / M_w$ vs. $M_w^{1/5}$ plots at high M_w based on the asymptotic relation^{14,23} $\alpha_s^2 = 1.53z_2^{2/5}$ (see ref 24 for the procedure). With these parameter values, α_s^2 vs. $\tilde{z}$ relations were obtained from the present and literature data^{3,4,12,16} for $\langle S^2 \rangle_z$ and M_w .

The results are displayed in Figure 8, in which the values of α_s^2 obtained with the aid of the experimental relation $\langle S^2 \rangle_{0z} = 1.00 \times 10^{-17} M_w \text{ cm}^2$ in IAIV⁴ are included; they are

Figure 8. Plots of α_s^2 vs. $\tilde{z}$ for PIB in heptane and in CH. The symbols are the same as those in Figure 7 (see the text for the meaning of pips). The solid curve represents eq 7.

one circle with pip (in heptane) and three squares with pip (in CH). All the plotted points are seen to fall essentially on a single curve, being consistent with the YSS scheme or the quasi two-parameter theory. Actually, this curve represents the values calculated from the Domb-Barrett function²⁵

$$\begin{aligned} \alpha_s^2 &= \left[1 + 10\tilde{z} + \left(\frac{70\pi}{9} + \frac{10}{3} \right) \tilde{z}^2 + 8\pi^{3/2} \tilde{z}^3 \right]^{2/15} \\ &\quad \times [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \end{aligned} \quad (7)$$

which reduces to the original Domb-Barrett equation in the coil limit. We note that the stiffness effect on the excluded-volume parameter amounts to 13% for the lowest-molecular weight fraction S-114B in CH.

We next discuss the interpenetration function Ψ defined by

$$\Psi = \frac{A_2 M^2}{4\pi^{3/2} N_A \langle S^2 \rangle^{3/2}} \quad (8)$$

where N_A is the Avogadro constant. The values of Ψ in heptane calculated from the data in Table I are shown by circles in Figure 9, along with those of Matsumoto *et al.*¹² in the same solvent (the triangles) and Nakamura *et al.* in

Figure 9. Plots of Ψ vs. α_s^3 for PIB in heptane and in CH. The symbols are the same as those in Figure 7. The dashed line represents the two-parameter theory values calculated from the Barrett equation.²⁶

CH (the squares). Our Ψ values in heptane and those of Matsumoto *et al.* come close to each other and are about 0.22 almost independent of α_s^3 over the molecular weight range studied. The data in CH appear systematically above those in heptane, revealing the breakdown of the two-parameter theory which predicts Ψ to be a universal function of α_s^3 .²⁰ As an example, the two-parameter theory values calculated from the Barrett equation²⁶ for $\Psi[(z_2/\alpha_s^3)(1 + 14.3z_2 + 57.3z_2^2)^{0.2}]$ and the Domb-Barrett equation for α_s (eq 7 in the coil limit) have been shown by a dashed line in the figure.

Recently, Yamakawa⁷ incorporated chain stiffness into Ψ in the same way as that for α_s (*i.e.*, with the helical wormlike chain), and showed that Ψ is no longer a universal function of α_s but depends separately on B_2 and M . In particular, his theory predicts that Ψ in a good solvent increases with decreasing α_s^3 , while in an intermediate solvent it is systematically lower than that in the good solvent and is insensitive to α_s^3 (see Figure 1 of ref 7). In his subsequent work, Yamakawa and collaborators⁸ substantiated these theoretical predictions by light scattering measurements on polystyrene in various solvents. The present

data for PIB in Figure 9 also conform to the predictions, lending additional support to the validity of the Yamakawa theory. In other words, the stiffness effect on the Ψ vs. α_s^3 relation is remarkable even at α_s^3 as large as 5. It should be pointed out, however, that in order to fit the theory to the Ψ data in heptane and CH, we must choose B_2 values about three times as large as those determined above from α_s^2 . As remarked by Yamakawa *et al.*,⁸ the theory for A_2 is semiquantitative.

Reduced Third Virial Coefficient

In previous work, Norisuye *et al.*⁵ introduced approximately effects of chain stiffness and ternary cluster interactions into the two-parameter theory of Stockmayer and Casassa²⁷ for g . The former effect was evaluated for the wormlike bead chain in the binary cluster approximation and the latter effect, in the first-order perturbation approximation. The result is expressed by a sum of the binary cluster contribution g_2 and the ternary cluster contribution g_3 , *i.e.*,

$$g = g_2 + g_3 \quad (9)$$

$$g_2 = \frac{2.22\hat{z}}{(1 + 18\hat{z} + 12.6\hat{z}^2)^{1/2}} \quad (10)$$

$$g_3 = \frac{4B_3}{3B_2^2\lambda L} \quad (11)$$

with

$$\hat{z} = \left(\frac{C}{2.22} \right) \left(\frac{z_2}{\alpha_s^3} \right) \quad (12)$$

Here, B_3 is the dimensionless parameter defined by $\beta_3\lambda^3/l^3$ with β_3 the ternary cluster integral for beads and C is a known function of λL and a cutoff parameter (see Figure 1 of ref 5). In the coil limit, C becomes equal to 2.22, so that $\hat{z}$ reduces to z_2/α_s^3 . As in our previous work,⁵ we take the cutoff parameter to be 0.3.

Values of g for heptane and CH solutions were calculated as functions of α_s^3 from the above expressions with eqs 4–7 for the para-

Figure 10. Comparison between experimental and theoretical values for g of PIB: unfilled circles, in heptane at 25°C; squares, in CH at 25°C;³ filled circles, in IAIV at 37°C;⁴ solid line, calculated values for heptane solutions; dashed line, calculated values for CH solutions; dotted line, calculated values for IAIV solutions; dot-dash line, two-parameter theory values.

meter sets: $B_2=0.08$ for heptane, $B_2=0.22$ for CH, and $M_L=241\text{ nm}^{-1}$, $\lambda^{-1}=1.4\text{ nm}$, and $B_3=0.021$ for both. The last parameter value was estimated from the relation $A_3=(N_A^2/3M_L^3\lambda^3)B_3$ at the theta point with the A_3 data⁴ ($A_3=5\times 10^{-4}\text{ mol g}^{-3}\text{ cm}^6$) for PIB in IAIV at 27°C on the assumption that B_3 is independent of solvent condition.

In Figure 10, the calculated g values for heptane and CH solutions are shown by solid and dashed lines, respectively, in comparison with the experimental data. The dot-dash line represents the two-parameter theory values, *i.e.*, the g_2 vs. α_S^3 relation without chain stiffness. Each of the abscissa values for a few lowest molecular weight fractions (three in heptane and two in CH) is the mean of α_S^3 obtained by extrapolating the $\langle S^2 \rangle_z$ data in Figure 7 and that calculated from eq 7. Even with some ambiguity of the abscissa values for those fractions, the following points may be made from the comparison between theory and experiment.

(1) The solid or dashed line fits the data

points for both heptane and CH solutions in the region of α_S^3 above 3, in which the two curves almost merge with the dot-dash line. Hence the two-parameter theory holds in this α_S^3 region. (2) As α_S^3 approaches unity, the dot-dash line abruptly goes down to zero, whereas the heptane data stay almost constant. This discrepancy confirms the previous conclusion⁵ (derived for good solvent systems) that the two-parameter theory breaks down for α_S^3 below 1.7. The failure of the theory in this α_S^3 region for heptane solutions is attributable primarily to the neglect of ternary cluster interactions, since the g_2 vs. α_S^3 relation with the effect of chain stiffness (not shown in the figure) comes only slightly above the dot-dash line for $\alpha_S^3 < 2$; the stiffness effects on g_2 and α_S^3 contribute toward lowering and raising the g_2 vs. α_S^3 curve, respectively,⁵ and these opposite contributions, along with the small B_2 value (see Figure 2 of ref 5), lead to the less pronounced stiffness effect on the curve for heptane. The essentially constant values of experimental g in heptane (for $\alpha_S^3 < 1.7$) may be explained as the result of a compensation of an increase in g_3 and a decrease in g_2 with decreasing α_S^3 . (3) However, the solid curve deviates downward from the heptane data for α_S^3 between 1.2 and 2, indicating that the theory of Norisuye *et al.*⁵ with the assigned parameter values considerably underestimates g for heptane solutions in the α_S^3 range. The theoretical g for heptane is larger than that for CH below $\alpha_S^3 \sim 1.2$, but experimentally, this occurs in a region of much larger α_S^3 . Though there remains some room to adjust the B_3 values in the two solvents, the theory is not quantitative.

Because of the lack of g data at low molecular weights, the present study fails to check the theoretical prediction that g abruptly increases when α_S^3 approaches unity. According to eq 9 with eq 11, however, such an abrupt increase in g should be observed even in an ordinary M_w range if the solvent conditions are made much poorer so that B_2 becomes much smaller

(see eq 11). This is shown to be indeed the case in the insert of Figure 10, in which, as an example, the previous data⁴ of g for PIB fractions S-14B, A-22B4, A-42B3, and A-62B1 ($M_w = 1.78 \times 10^5 - 1.60 \times 10^6$) in IAIV at 37°C (the filled circles) are compared with the theoretical values (the dotted line) for $B_2 = 0.004$ and the same parameter values for M_L , λ^{-1} , and B_3 as those in heptane or CH. The B_2 value has been determined so that eq 7 leads to the closest agreement with the α_S^2 data.⁴ As expected, the experimental g values (0.76–1.7) in IAIV are much larger than those in heptane. Further, their agreement with the theoretical values (the dotted line) is not bad.

CONCLUSIONS

The present data for A_2 and A_3 of PIB in heptane, when combined with the previous data in cyclohexane, give additional evidence for the breakdown of the two-parameter theory. The behavior of Ψ in the two solvents can be explained semiquantitatively by the Yamakawa theory⁷ that takes into account the effect of chain stiffness in the binary cluster approximation. On the other hand, the binary cluster approximation with the stiffness effect does not hold for g unless α_S^3 is larger than about 1.7. For $\alpha_S^3 < 1.7$, the effect of three-segment interactions on g (and hence on A_3) cannot be ignored, and the contribution of such interactions to g increases as α_S^3 decreases or the solvent quality becomes poorer. Though qualitatively, the observed behavior of g for PIB is explained by the recent theory of Norisuye *et al.*⁵

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