Effects of Three-Segment Interactions on the Temperature Dependence of the Third Virial Coefficient for Flexible Chains near the Θ Point

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ABSTRACT: The third virial coefficient A_3 of long flexible chains with three-segment interactions is evaluated perturbatively to third order in the ternary segment cluster integral β_3 to explain the recent experimental finding on polystyrene and polyisobutylene that A_3 has a positive minimum around the Θ temperature (where the second virial coefficient A_2 is zero) in contrast to the prediction from the two-parameter theory. The calculation indicates that A_3 near the Θ point is determined by two functions. One corresponds to the two-parameter theory, but the binary cluster integral β_2 is replaced by an effective binary cluster integral β_e, i.e., by a linear combination of the binary and ternary cluster integrals. The other is a decreasing function of β_e, multiplied by β_3, and it reduces to β_3 at the Θ point. The sum of these two functions is shown to give A_3 a positive minimum around the Θ temperature, in accord with the experimental finding mentioned above. Thus, the experimentally observed increase in A_3 with a decrease in temperature below Θ is due to a marked effect of three-segment interactions. It is also shown that the second virial coefficient, which is readily derived from the calculation of A_3 up to second order in β_2 and β_3, contains no separate term dependent on β_3 and is a function of β_e up to at least second order. This indicates that in practice the binary cluster approximation holds for A_2 of long flexible chains near Θ even when the ternary cluster contribution is not negligible.

Introduction

The two-parameter theory[1] predicts that the third virial coefficient A_3 for linear flexible chains vanishes at the Θ point and becomes negative below it. In contrast to this prediction, our recent light scattering studies on polystyrene[2] and polyisobutylene[3] in Θ solvents showed that A_3 remains positive at T = Θ and rather increases when the temperature T is lowered below Θ. Here, the Θ point is defined as the temperature at which the second virial coefficient A_2 vanishes. The apparent breakdown of the two-parameter theory for A_3 near Θ is most likely due to the neglect of three-segment interactions.

In the present work, with such interactions taken into account, we carried out elementary perturbation calculations on A_3 of linear flexible chains to third order in the ternary segment cluster integral β_3, hoping to explain the temperature dependence observed for polystyrene and polyisobutylene near the Θ temperature. The calculation was confined to infinitely long chains that obey the Gaussian statistics in the unperturbed state.

Perturbation Calculations

If both β_2 (the binary cluster integral) and β_3 are vanishingly small, A_3 in the superposition approximation[1] may be expanded in powers of β_2 and β_3 as

$$A_3 = \frac{{N_A}^2 n^3}{3M^3}\{\beta_3 - I_1\beta_2\beta_3 - I_2{\beta_3}^2 + J_1{\beta_2}^3 + J_2{\beta_2}^2\beta_3 + J_3\beta_2{\beta_3}^2 + J_4{\beta_3}^3 + ...\} \quad (1)$$

Here, M is the molecular weight of each chain containing n segments and N_A is the Avogadro constant. The leading term results from[4,5]

$$\beta_3 n^{-3} \sum\sum_{i_1,j_2,k_3}\sum P(O_{i_1j_2k_3})$$

where $P(O_{i_1j_2k_3})$ represents the probability density that segment i_1 in chain 1, segment j_2 in chain 2, and segment k_3 in chain 3 are in contact. The coefficient J_1 corresponds to the first-order term in the binary cluster approximation. It is already known to be[6,7]

$$J_1 = n^{-3} \sum\sum_{i_1,j_2,k_2,l_3,s_1,t_3}\cdots\sum\sum P(O_{i_1j_2},O_{k_2l_3},O_{s_1t_3}) = \lambda_1(3/2\pi b^2)^{3/2}n^{3/2} \quad (2)$$

with

$$\lambda_1 = 1.664 \quad (3)$$

and b the effective bond length.

We evaluated I_1, I_2, J_2, J_3, and J_4 in the limit of infinite n, with sums replaced by integrals and with a cutoff parameter σ ($n \gg \sigma > 0$) introduced for mathematical tractability. The results read

$$I_1 = 3n^{-3} \sum\sum_{i_1,j_2,k_3,s_1,t_2}\cdots\sum\sum P(O_{i_1j_2k_3},O_{s_1t_2}) = 6C_1(3/2\pi b^2)^{3/2}n^{1/2} \quad (4)$$

$$I_2 = 6n^{-3} \sum\sum_{i_1,j_2,k_3,s_1<t_1,u_2}\cdots\sum\sum P(O_{i_1j_2k_3},O_{s_1t_1u_2}) = 6C_1(4/\sigma^{1/2})(3/2\pi b^2)^3 n^{1/2} \quad (5)$$

$$J_2 = 6n^{-3} \sum\sum_{i_1<j_1,k_2,s_1,t_3,u_2,v_3}\cdots\sum\sum P(O_{i_1j_1k_2},O_{s_1t_3},O_{u_2v_3}) = 3\lambda_1(4/\sigma^{1/2})(3/2\pi b^2)^3 n^{3/2} \quad (6)$$

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$$J_3 = 3n^{-3}\Big[\sum\sum\cdots\sum\sum_{i_1<j_1,k_2,s_1<t_1,l_3,u_2,v_3} P(\mathrm{O}_{i_1j_1k_2},\mathrm{O}_{s_1t_1l_3},\mathrm{O}_{u_2v_3}) + \sum\sum\cdots\sum\sum_{i_1<j_1,k_2,s_3<t_3,l_2,u_1,v_3} P(\mathrm{O}_{i_1j_1k_2},\mathrm{O}_{s_3t_3l_2},\mathrm{O}_{u_1v_3}) + 2\sum\sum\cdots\sum\sum_{i_1<j_1,k_2,s_2<t_2,l_3,u_1,v_3} P(\mathrm{O}_{i_1j_1k_2},\mathrm{O}_{s_2t_2l_3},\mathrm{O}_{u_1v_3})\Big] = 3\lambda_1(4/\sigma^{1/2})^2(3/2\pi b^2)^{9/2}n^{3/2} \quad (7)$$

$$J_4 = 2n^{-3}\Big[3\sum\sum\cdots\sum\sum_{i_1<j_1,k_2,s_1<t_1,l_3,u_2<v_2,w_3} \times P(\mathrm{O}_{i_1j_1k_2},\mathrm{O}_{s_1t_1l_3},\mathrm{O}_{u_2v_2w_3}) + \sum\sum\cdots\sum\sum_{i_1<j_1,k_2,l_1,s_3<t_3,u_2<v_2,w_3} \times P(\mathrm{O}_{i_1j_1k_2},\mathrm{O}_{l_1s_3t_3},\mathrm{O}_{u_2v_2w_3})\Big] = \lambda_1(4/\sigma^{1/2})^3(3/2\pi b^2)^6 n^{3/2} \quad (8)$$

where C_1 is given by

$$C_1 = 2.865 \quad (9)$$

which is the well-known coefficient[1,4] of the double-contact term of A_2 in the two-parameter theory. Two points should be noted here. First, intramolecular excluded volume does not affect I_1, I_2, J_2, J_3, and J_4 in the limit of infinite n. Second, J_2, J_3, and J_4 originally contain many terms associated with $\sum\ldots\sum P(\mathrm{O}_{i_1j_2k_3},\ldots)$ including intramolecular excluded-volume contributions such as $n^{-3}\sum\ldots\sum[P(\mathrm{O}_{i_1j_2k_3},\mathrm{O}_{s_1t_2},\mathrm{O}_{u_1v_1}) - P(\mathrm{O}_{i_1j_2k_3},\mathrm{O}_{s_1t_2})P(\mathrm{O}_{u_1v_1})]$, but these terms give values of order n (see eq 11).

Substituting the above expressions for I_1, ..., J_4 into eq 1, we obtain

$$A_3 = \frac{N_A{}^2n^3}{3M^3}[\beta_3H(Z) + (2\pi b^2/3)^3K(Z)] \quad (10)$$

where

$$H(Z) = 1 - 6C_1Z + \mathcal{O}(Z^2) \quad (11)$$

$$K(Z) = \lambda_1Z^3 + \ldots \quad (12)$$

and

$$Z = (3/2\pi b^2)^{3/2}\beta_e n^{1/2} \quad (13)$$

with β_e an effective binary cluster integral defined by

$$\beta_e = \beta_2 + (4/\sigma^{1/2})(3/2\pi b^2)^{3/2}\beta_3 \quad (14)$$

The last term $\mathcal{O}(Z^2)$ in eq 11 comes from J_2, J_3, and J_4 all containing $n^{-3}\sum\ldots\sum P(\mathrm{O}_{i_1j_2k_3},\ldots)$ and is always positive. Though, in the limit of infinite n, this term can be neglected in comparison to $\lambda_1(2\pi b^2/3)^3Z^3$, it is important to note that $H(Z)$ arises necessarily from the configurations with contact of three segments i_1, j_2, and k_3 in the three different chains and is a Z-expansion different in order of n from $K(Z)$. The leading term of the latter [i.e., $\lambda_1(2\pi b^2/3)^3Z^3$] with $\beta_e = \beta_2$ is just the first-order term in the binary cluster approximation,[6,7] whereas $\beta_3H(Z)$ is completely ignored in this approximation. With regard to the effective binary cluster integral, the following remarks may be in order.

If the sums in eqs 5–8 are asymptotically evaluated, it is found that $2\sigma^{-1/2}$ is replaced by $\zeta(3/2)$ (=2.612), with $\zeta(x)$ being the Riemann ζ function of variable x. Thus, in the discrete random flight chain model, σ is slightly smaller than unity. However, a value much larger than unity must be taken for it[8] when chain stiffness is incorporated with the wormlike[9,10] or helical wormlike[11,12] bead model. In all cases, the effective binary cluster integral very near Θ is a sum of β_2 and $C\beta_3$, though the constant C differs depending on the model or the mathematical approximation employed. Since σ does not explicitly appear in eqs 10–13, its precise value is unnecessary for the present purpose.

The present calculation also gives A_2 for infinitely long chains up to second order in both β_2 and β_3, since the basic equation for A_3 contains $4A_2{}^2M$ (see eq 22.5 of ref 1). The first-order terms of β_2 and β_3 are already known[2,5,13] but the second-order calculation is new. The result obtained is written in the form

$$A_2 = \frac{N_An^2}{2M^2}\beta_e h(Z) \quad (15)$$

$$h(Z) = 1 - C_1Z + \ldots \quad (16)$$

Importantly, eq 15 with eq 16 and $\beta_e = \beta_2$ is identical to the familiar expression in the two-parameter theory[1] at least up to $\mathcal{O}(\beta_e{}^2)$, showing that the Θ point for sufficiently long chains is the temperature at which β_e vanishes. Under this condition, eq 10 reduces to

$$A_3 = (N_A{}^2n^3/3M^3)\beta_3 \quad \text{(at the Θ point)} \quad (17)$$

so that a positive A_3 at the Θ temperature corresponds to a positive β_3. In previous work,[2,3] we used this equation to estimate β_3 from A_3 data for polystyrene and polyisobutylene at the Θ temperature. Another point to note is that there is a close relation between $H(Z)$ and $h(Z)$ for very small Z. In fact, $n^{-3}\sum\ldots\sum P(\mathrm{O}_{i_1j_2k_3},\mathrm{O}_{s_1t_1u_2})$ in eq 5 becomes identical to $n^{-2}\sum\ldots\sum P(\mathrm{O}_{i_1j_2},\mathrm{O}_{s_1t_1u_2})$ appearing in the $\beta_2\beta_3$ term of A_2 (not shown here) when the sum over k_3 is taken; the factor 6 in $H(Z)$ arises from a larger number of distinguishable configurations available for 3 chains.

Discussion

For convenience of our discussion, the previously reported A_3 data for different samples of polystyrene in cyclohexane (Θ = 34.5 °C)[2] and of polyisobutylene in isoamyl isovalerate (Θ = 27 °C)[3] are reproduced as functions of T in Figures 1 and 2, respectively. For both polymers the curve of A_3 vs T is nearly parabolic with a broad, positive minimum around Θ and becomes almost horizontal as M decreases. Thus A_3 below Θ is strongly M-dependent, and, in particular, its rise with a decrease in T is opposite to the two-parameter theory prediction, as already mentioned in the Introduction. Our purpose here is to explain these features of the A_3 vs T curves on the basis of eq 10.

If β_2 varies linearly with T^{-1} and if β_3 is independent of T, the effective binary cluster integral defined by eq 14 may be expressed as[14]

$$\beta_e = \beta_0[1 - (\Theta/T)] \quad (18)$$

where β_0 is a constant independent of T. This equation with $\beta_e = \beta_2$ is the one usually assumed for data analysis within the framework of two-parameter theory. When β_0 is positive (as is the case for the two polymer + solvent systems in Figures 1 and 2), β_e and hence Z are negative for $T < \Theta$, so that for a positive β_3, $\beta_3H(Z)$ in eq 10 is positive below Θ and is a sharply decreasing function of T. Equation 10 indicates that A_3 near Θ is a sum of this function and $\lambda_1(2\pi b^2/3)^3Z^3$, corresponding to the leading term in the two-parameter theory. Since the latter is an

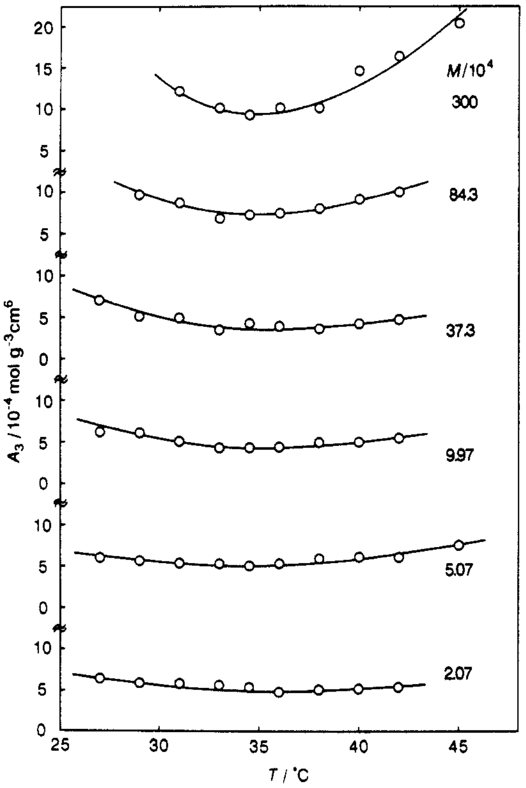

Figure 1. Temperature dependence of A_3 for polystyrene samples in cyclohexane (Θ = 34.5 °C).

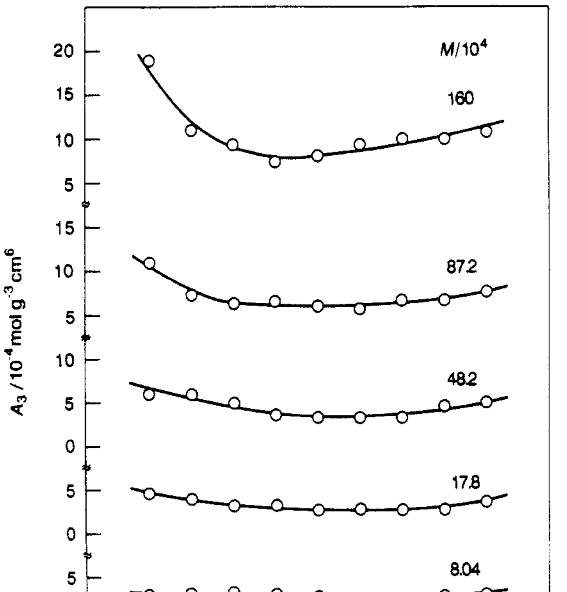

Figure 2. Temperature dependence of A_3 for polyisobutylene samples in isoamyl isovalerate (Θ = 27 °C).

increasing function of T giving zero at $T = \Theta$, the sum of these two functions opposite with respect to a change in T may give A_3 a positive minimum somewhere around Θ. It may also be anticipated that since $|Z|$ stays smaller for a smaller n in a given T range, the temperature dependence of A_3 should become weaker as M decreases. These are our interpretation of the features of the experimental A_3 vs T curves in Figures 1 and 2 and are shown below to be the case in a semiquantitative way by using appropriate closed expressions for $H(Z)$ and $K(Z)$.

Since $H(Z)$ for small Z has a close relation to the h function appearing in A_2, it may fairly well be approximated by $h(6Z)$ in the vicinity of the Θ point. We adopt the Casassa–Markovitz h function[15] in the two-parameter A_2 theory, assuming, for simplicity, that the expansion factor for the chain expansion due to intramolecular excluded-volume effects is equal to unity over the ranges of T and M of interest, i.e.,

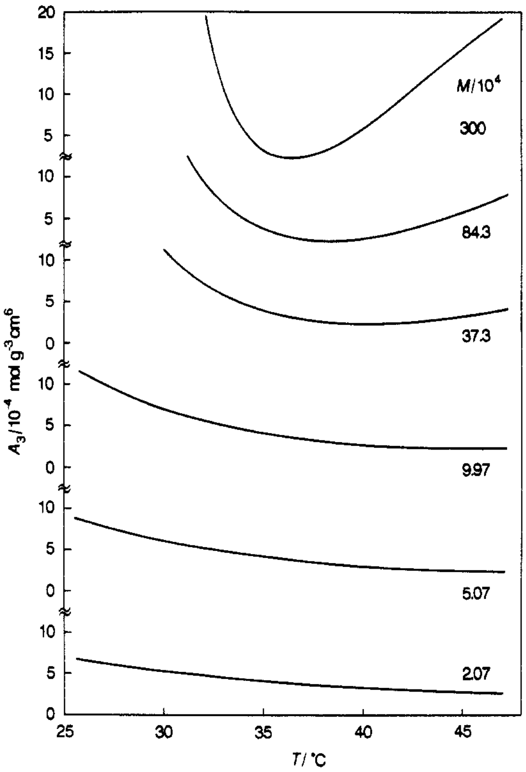

Figure 3. Theoretical curves of A_3 vs T calculated from eq 10 with eqs 13, 18, 19, and 20 for polystyrene in cyclohexane. See the text for the parameter values used.

$$H(Z) = \frac{1 - \exp(-12C_1Z)}{12C_1Z} \tag{19}$$

This gives the correct first-order coefficient $6C_1$ in eq 11. Its advantage is that it has a solution for negative Z, differing from other available h functions.[1,16–18] For $K(Z)$, we use Yamakawa's two-parameter theory[7] for A_3, with the expansion factor again assumed to be unity. We thus have

$$K(Z) = [1 - \exp(-\lambda_1Z)][1 - \exp(-2C_1Z)]^2/(2C_1)^2 \tag{20}$$

Though the Yamakawa theory overestimates A_3 in good solvents,[19–21] it gives the correct coefficient λ_1 at small Z and has a solution for $Z < 0$.

Figures 3 and 4 show the curves of A_3 vs T computed as functions of M from eq 10 with eqs 13, 18, 19, and 20 using b = 0.74 nm, $\beta_0 = 7.2 \times 10^{-23}$ cm^3, and $\beta_3 = 4 \times 10^{-45}$ cm^6 for polystyrene in cyclohexane and b = 0.58 nm, $\beta_0 = 1.4 \times 10^{-23}$ cm^3, and $\beta_3 = 7 \times 10^{-46}$ cm^6 for polyisobutylene in isoamyl isovalerate. The values for β_0 have been taken from the paper of Miyaki and Fujita[22] and those for β_3 from our previous papers.[2,3] It can be seen that the calculated curve for the highest molecular weight sample of either polymer has a pronounced minimum around Θ (more precisely, at a T slightly higher than Θ), rising with decreasing T below Θ. As M decreases, the curve becomes nearly flat. These features of the theoretical curves closely resemble those observed in Figures 1 and 2. We may therefore conclude that the experimentally observed increases in A_3 with lowering T below Θ are due to the

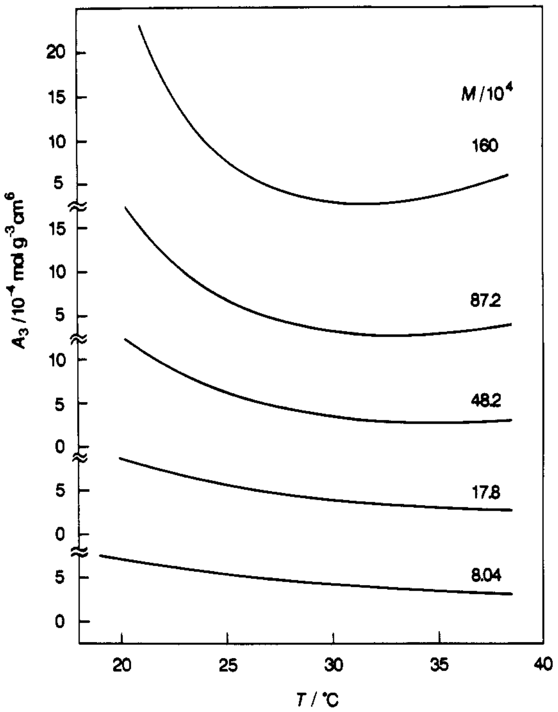

Figure 4. Theoretical curves of A_3 vs T calculated from eq 10 with eqs 13, 18, 19, and 20 for polyisobutylene in isoamyl isovalerate. See the text for the parameter values used.

nontrivial contribution of $\beta_3 H(Z)$ ignored in the binary cluster approximation. This is probably the first exemplification of a remarkable effect of three-segment interactions on dilute solution properties.

A few theoretical curves for lower molecular weights in Figures 3 and 4 continue to decline gradually with increasing T even above Θ. Though this behavior differs somewhat from the experimental dependence, the difference does not seem serious in terms of the present semiquantitative analysis. Actually, the declines of the theoretical curves for T above Θ are a reflection of the fact that the calculated A_3 for high M has a minimum at a T slightly above Θ, and thus any of the theoretical curves rises at high T where $(2\pi b^2/3)^3 K(Z)$ surpasses $\beta_3 H(Z)$. The contribution of the latter to A_3 indeed diminishes to less than 10% for either of the polymers when Z exceeds 0.2.

Concluding Remarks

The present calculation of A_3 for long flexible chains with three-segment interactions explains at least qualitatively the observed temperature dependence of A_3 for polystyrene[2] and polyisobutylene[3] in Θ solvents, demonstrating that the ternary cluster interaction plays an essential role in A_3 near the Θ temperature. It is thus legitimate to consider effects of β_3 on other dilute-solution properties of flexible chains.

Equation 15 with eq 16 shows that A_2 near Θ has no separate term associated with β_3 and is determined only by the effective binary cluster integral β_e. This is also the case for the expansion factor[14] of the end-to-end distance up to $\mathcal{O}(\beta_e^2)$ (and probably for the radius expansion factor α_s).[23] These theoretical results indicate that the binary cluster approximation should be accurate enough for A_2 and α_s of long chains provided β_2 is replaced by β_e.[24] This explains why three-segment interactions need not be considered explicitly for these properties. In other words, consideration of β_3 gives a consistent explanation of α_s, A_2, and A_3 for long flexible chains. A similar conclusion was drawn recently by Yamakawa,[8] who explicitly considered effects of chain stiffness on α_s and A_2 (see ref 25 for A_3 in good solvents). He further argued that all terms associated with β_3 may be neglected compared to β_2 as far as α_s and A_2 are concerned. This is the case for stiff chains,[8] but the remarks made below for usual flexible chains supplement his argument for the ternary cluster contribution to β_0 (the temperature-independent part of β_e).

Yamakawa[8] estimated this contribution to be at most 5% for polystyrene in cyclohexane by taking account of the chain stiffness with the helical wormlike chain model.[11,12] For polyisobutylene in isoamyl isovalerate,[3] the corresponding contribution is estimated to be 10%, which is somewhat larger than the value for polystyrene, probably because the polyisobutylene chain is more flexible.[26] These contributions are small (compared to β_0), as argued by Yamakawa,[8] but they cannot be ignored compared to β_2 or β_e in the vicinity of the Θ temperature, especially when β_2 approaches zero at a certain temperature close to Θ. The point we wish to make here is that, since the sum of the binary and ternary cluster contributions, i.e., β_e, is the key parameter in the vicinity of the Θ point, the magnitude of the ternary cluster contribution to β_e is immaterial for properties of long flexible chains other than A_3. As the present study shows, only A_3 contains a separate function of β_3, i.e., $\beta_3 H(Z)$ in eq 10.

References and Notes

(1) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(2) Nakamura, Y.; Norisuye, T.; Teramoto, A. *Macromolecules* **1991**, *24*, 4904.
(3) Akasaka, K.; Nakamura, Y.; Norisuye, T.; Teramoto, A. *Polym. J.* **1994**, *26*, 363.
(4) Zimm, B. H. *J. Chem. Phys.* **1946**, *14*, 164.
(5) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1985**, *83*, 5293.
(6) Stockmayer, W. H. *Makromol. Chem.* **1960**, *35*, 54.
(7) Yamakawa, H. *J. Chem. Phys.* **1965**, *42*, 1764.
(8) Yamakawa, H. *Macromolecules* **1993**, *26*, 5061.
(9) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 1106.
(10) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972**, *57*, 2843.
(11) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1984**, *35*, 23.
(12) Shimada, J.; Yamakawa, H. *J. Chem. Phys.* **1986**, *85*, 591.
(13) Yamakawa, H. *J. Chem. Phys.* **1966**, *45*, 2606.
(14) Norisuye, T.; Nakamura, Y. *Polymer* **1993**, *34*, 1440.
(15) Casassa, E. F.; Markovitz, H. *J. Chem. Phys.* **1958**, *29*, 493.
(16) Tanaka, G.; Šolc, K. *Macromolecules* **1982**, *15*, 791.
(17) Barrett, A. J. *Macromolecules* **1985**, *18*, 196.
(18) Freed, K. *Renormalization Group Theory of Macromolecules*; Wiley-Interscience: New York, 1987.
(19) Nakamura, Y.; Norisuye, T.; Teramoto, A. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 153.
(20) Norisuye, T.; Fujita, H. *ChemTracts—Macromol. Chem.* **1991**, *2*, 293.
(21) Nakamura, Y.; Akasaka, K.; Katayama, K.; Norisuye, T.; Teramoto, A. *Macromolecules* **1992**, *25*, 1134.
(22) Miyaki, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 742.
(23) The second-order calculation is yet unavailable.
(24) According to Yamakawa,[8] the constant C in the equation $\beta_e = \beta_2 + C\beta_3$ for α_s differs from that for A_2 when chain stiffness is introduced, but the difference may give no serious problem.
(25) Norisuye, T.; Nakamura, Y.; Akasaka, K. *Macromolecules* **1993**, *26*, 3791.
(26) Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1991**, *24*, 4423.