Ternary Cluster Integral for Polystyrene in *trans*-Decalin near the Θ Point

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Received August 13, 1996⊗

ABSTRACT: Light scattering measurements have been made on 10 polystyrene samples with weight-average molecular weights M_w of 1.2×10^3 to 3.1×10^6 in *trans*-decalin at temperatures T between 13 and 55 °C to determine the second and third virial coefficients (A_2 and A_3) as functions of M_w and T. The former coefficient at the Θ point (21 °C), where it vanishes for high M_w, is found to become negative and then sharply increase to positive with decreasing M_w. This molecular weight dependence of A_2 is similar to that recently observed for atactic poly(methyl methacrylate) in acetonitrile at the Θ temperature. The data of A_3 for high M_w plotted against T have a broad positive minimum around the Θ point in contrast to the two-parameter theory prediction that A_3 vanishes at Θ and becomes negative below Θ, thus demonstrating the breakdown of the binary cluster approximation to A_3 of polystyrene in *trans*-decalin near Θ. For low molecular weights, A_3 is insensitive to T and larger for lower M_w. The latter feature is ascribable to the effect from chain ends. From an analysis of the A_3 data for low M_w at T between 17 and 35 °C the ternary cluster integral is estimated to be about 4×10^{-45} cm^6, almost regardless of T. Its T-insensitive behavior bears some analogy with the temperature dependence of the third virial coefficient for imperfect monatomic gases near the Boyle point.

Introduction

The two-parameter theory[1] predicts that the third virial coefficient A_3 for linear flexible polymers vanishes at the Θ point and becomes negative below Θ. In contrast to this prediction, our recent light scattering work[2,3] on high molecular weight polystyrene in cyclohexane and polyisobutylene in isoamyl isovalerate showed that A_3 remains positive at Θ and rather increases with lowering temperature T below Θ. In a more recent study,[4] we theoretically explained this finding as due to an effect of three-segment interactions. Although the nonvanishing of A_3 at the Θ temperature is now known for several flexible polymer + solvent systems,[2,3,5−7] the experimental study on the T dependence of A_3 near Θ is yet limited to the two systems mentioned above.

The present paper reports a light scattering study made on polystyrene in *trans*-decalin as an extension of our previous experimental work.[2,3] Its purpose is twofold: one is to ascertain that A_3 for this system near Θ also exhibits behavior predictable from our previous theoretical calculation[4] on long chains with three-segment interactions, and the other is to determine the ternary cluster integral β_3 as a function of T from A_3 data for low molecular weights. For the latter purpose, use of very low molecular weight samples including oligomers may be desirable since the contribution from *double* and higher-order segment contacts to A_3 should be small for such samples. However, our light scattering measurement was confined to molecular weights above 10^3 so that the scattering intensity arising from density fluctuation can be replaced by that for a pure solvent.[8−10] In the work reported below, a procedure for estimating β_3 from A_3 data is described and then light scattering results and their analysis are presented.

Theoretical Considerations

For the purpose of estimating β_3, we here derive an expression of A_3 relevant to analysis of data for short chains near the Θ point by first considering flexible chains and then incorporating chain stiffness and end effects.

Long Chains. According to our previous perturbation calculation[4] based on the random flight model, A_2 (the second virial coefficient) and A_3 for long, linear flexible chains with small binary and ternary interactions are expressed by

$$A_2 = \left(\frac{N_A}{2{M_0}^2}\right)\beta h(z) \tag{1}$$

$$A_3 = \left(\frac{{N_A}^2}{3{M_0}^3}\right)\left[\beta_3 H(z) + \left(\frac{2\pi b^2}{3}\right)^3 I(z)\right] \tag{2}$$

where

$$h(z) = 1 - C_1 z + O(z^2) \tag{3}$$

$$H(z) = 1 - 6C_1 z + O(z^2) \tag{4}$$

$$I(z) = 1.664z^3 + ... \tag{5}$$

and

$$z = [3/(2\pi b^2)]^{3/2}\beta n^{1/2} \tag{6a}$$

with $C_1 = 2.865$ and β the effective binary cluster integral defined by $\beta = \beta_2 + C\beta_3$. In these equations, N_A is the Avogadro constant, M_0 is the molar mass of the monomer, b is its effective length, n is the degree of polymerization, and β_2 is the binary cluster integral; C is a constant for the polymer + solvent system considered, but its expression differs depending on the chain model or mathematical approximation employed.[4,11] Equations 3 and 5 are equivalent to the well-known z-expansions of A_2 and A_3 in the two-parameter scheme,[1] and moreover, the ternary cluster contribution $C\beta_3$ to β is considered small for actual polymer chains with finite stiffness[11] unless β_2 is vanishingly small. Thus the functions $h(z)$ and $I(z)$ near Θ can be regarded as

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⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1997.

substantially identical to those in the two-parameter theory. It is important to note, however, that the term $\beta_3 H(z)$ in A_3 is completely ignored in this theory.

At the Θ point where $A_2 = 0$ for high molecular weight M, β vanishes and eq 2 reduces to[12]

$$A_3(\Theta) = \left(\frac{N_A{}^2}{3M_0{}^3}\right)\beta_3 \tag{7}$$

This equation implies that $A_3(\Theta)$, i.e., A_3 at Θ, remains nonzero unless β_3 is zero.

Stiffness Effect. Equation 2 with eqs 4 and 5 (eq 1 with eq 3 as well) is applicable only to long enough chains near Θ because of the random flight model invoked. The effect of chain stiffness on the $I(z)$ function in eq 2 was studied previously[13] with the wormlike[14] or helical wormlike (HW)[15] bead model, as done by Yamakawa and Stockmayer[16] and by Yamakawa[17] for A_2, but it turned out to be small. More importantly, even the leading term of this function, associated with the *triple* contact, can be ignored in comparison to $\beta_3 H(z)$ for usual flexible chains provided that $|z| < 0.03$.

On the other hand, as eq 4 shows, $H(z)$ deviates appreciably from unity even for $z \approx 0.01$ because of the large negative first-order coefficient. The stiffness effect on this function may be approximately taken into account in the manner[17] employed for $h(z)$, since in the vicinity of the Θ point, these functions are closely related to each other, that is, $H(z) \approx h(6z)$; the factor 6 in the z-expansion of $H(z)$ arises from a larger number of distinguishable configurations available for three chains (see ref 4). We may thus replace z with $\tilde{\tilde{z}}$ appearing in the h function for the HW bead model, i.e., with the intermolecular scaled excluded-volume parameter defined by[17]

$$\tilde{\tilde{z}} = (Q/C_1)z \tag{8}$$

with z defined by

$$z = [3\lambda/(2\pi c_\infty a)]^{3/2}\beta(L/a)^{1/2} \tag{6b}$$

instead of eq 6a. Here, λ^{-1} is the stiffness parameter, L is the contour length, Q is a known function of λL approaching C_1 in the coil limit, a is the bead spacing, and c_∞ is defined by $c_\infty = 6\lambda\langle S^2\rangle_0/L$ for infinite L ($\langle S^2\rangle_0$ is the unperturbed mean-square radius of gyration of the HW chain). We have taken each monomer as one bead, so that the relation $b^2 = c_\infty a\lambda^{-1}$ holds. The contour length is related to M by $L = M/M_L$, with M_L being the molar mass per unit contour length.

Short Chains. As the chains get short, the effect of their ends on A_3 may become appreciable. Yamakawa et al.[6] evaluated all *single*-contact terms of the end contribution $A_3{}^{(E)}$ to A_3 and substantiated the significance of this effect for atactic polystyrene in cyclohexane and atactic poly(methyl methacrylate) (a-PMMA) in acetonitrile at the Θ temperature. Although their expression may be applicable to oligomers even at non-Θ temperatures, the *double*-contact terms of $A_3{}^{(E)}$ need to be examined for samples with molecular weights of the order 10^3. We thus calculated them by invoking the random flight model (see ref 4) and then incorporating the stiffness effect in the same way as above. For short chains, this approximate treatment is likely to overestimate the ternary cluster contributions to β and β' (see below for the definition), but it may introduce no serious error, since, as already noted, the ternary cluster contributions themselves should be small.

The result obtained in this way is written

$$A_3{}^{(E)} = 2N_A{}^2 M_0{}^{-2} M^{-1} \beta_{3,1} H^{(E)} \tag{9}$$

with

$$2\beta_{3,1} = \beta_{3,001} + \beta_{3,002} - 2\beta_{3,000} \tag{10}$$

$$H^{(E)} = 1 - (9/2)C_1\tilde{\tilde{z}} - (5/2)C_1(\beta_3/\beta_{3,1})\tilde{\tilde{z}}' \tag{11}$$

Here, $\beta_{3,00i}$ ($i = 0, 1, 2$) is the ternary cluster integral for the interaction among two intermediate beads and bead i, with i being zero for any intermediate bead (the subscript 0) and 1 or 2 for either of the end beads ($\beta_{3,000} = \beta_3$), and $\tilde{\tilde{z}}'$ is defined by eq 8 with eq 6b but with β' ($= \beta_{2,1} + C\beta_{3,1}$) in place of β; the excess binary cluster integral $\beta_{2,1}$ is defined by

$$2\beta_{2,1} = \beta_{2,01} + \beta_{2,02} - 2\beta_{2,00} \tag{12}$$

wherein $\beta_{2,0i}$ ($i = 0, 1, 2$) is the binary cluster integral for the interaction between an intermediate bead and bead i ($\beta_{2,00} = \beta_2$).

The desired A_3, which is the sum of eq 2 (with stiffness effect) and eq 9, may be expressed as

$$A_3/H = (N_A{}^2/3M_0{}^3)[\beta_3 + (6M_0\beta_{3,1}/M)(H^{(E)}/H)] \tag{13}$$

with

$$H^{(E)}/H = 1 + (3/2)C_1\tilde{\tilde{z}} - (5/2)C_1(\beta_3/\beta_{3,1})\tilde{\tilde{z}}' \tag{14}$$

where we have ignored the $I(z)$ function and abbreviated $H(\tilde{\tilde{z}})$ to H. Although the second and third terms in eq 14 contribute to $H^{(E)}/H$ more greatly for a higher molecular weight, their contributions to A_3 diminish to zero as M increases. Thus, β_3 at a given T can be estimated by extrapolation of A_3/H for low molecular weights to $M^{-1} = 0$. Practically, the function $H(\tilde{\tilde{z}})$ may be replaced by $h(6\tilde{\tilde{z}})$, but the analysis must be restricted to $H(\tilde{\tilde{z}})$ or $h(6\tilde{\tilde{z}})$ values close to unity so that several approximations involved in $H(\tilde{\tilde{z}})$ do not lead to significant errors in the estimation of β_3. An approximate value of $\beta_{3,1}$ (with an error of about 10%) can also be evaluated from the (initial) slope of the A_3/H vs M^{-1} plot if both $|\tilde{\tilde{z}}|$ and $|(\beta_3/\beta_{3,1})\tilde{\tilde{z}}'|$ are less than 0.01. We note that $\tilde{\tilde{z}}'$ does not always vanish at the Θ point.

Experimental Section

Samples and Preparation of Solutions. Ten atactic polystyrene fractions with molecular weights of 1.2×10^3 to 3.1×10^6 were used for the present study. Six of them, F288-B, F80-B, F-40B, 4a-B, F′4-B, and 2b-B, were chosen from the previously investigated samples.[2] The other fractions designated below as F-1b, A5000b, A2500b, and A1000a were obtained from Toso's standard samples F-1, A5000, A2500, and A1000, respectively, by fractional precipitation with benzene as the solvent and methanol as the precipitant. The weight-to number-average molecular weight ratios for F-1b, A5000b, and A2500b were 1.03, 1.07, and 1.05, respectively, when determined by gel-permeation chromatography.

A given polystyrene fraction was mixed with *trans*-decalin (Tokyo Kasei) under stirring at about 40 °C over one to several days depending on the molecular weight. The polymer mass concentration c was calculated from the gravimetrically determined weight fraction with the density ρ of the solution. The *trans*-decalin used was fractionally distilled under a reduced nitrogen atmosphere after being dehydrated with calcium hydride. Its *trans* content was determined to be 99.7% by gas chromatography.

Density measurements were made on samples F-40B ($c < 0.05$ g cm^{-3}), F-1b ($c < 0.10$ g cm^{-3}), A5000b ($c < 0.10$ g cm^{-3}), A2500b ($c < 0.15$ g cm^{-3}), and A1000a ($c < 0.19$ g cm^{-3}) in *trans*-decalin at 21, 25, 30, and 35 °C using bicapillary pycnometers of 5 or 30 cm^3 capacity. Necessary values of ρ were obtained by graphical interpolation or extrapolation of the data.

Light Scattering. Total intensity measurements on *trans*-decalin solutions of polystyrene were made at different temperatures T between 13 and 55 °C on a Fica 50 light scattering photometer in an angular range from 15 (or 45°) to 150°. Vertically polarized incident light of 436-nm wavelength was used for the four lowest molecular weight samples and that of 546 nm for the rest. The apparatus was calibrated with pure benzene at 25 °C, with the Rayleigh ratio (for unpolarized light at 90°) taken as 46.5×10^{-6} and 16.1×10^{-6} cm^{-1} for 436 and 546 nm, respectively. The depolarization ratio ρ_u of this liquid was determined to be 0.41 for 436 nm and 0.40 for 546 nm by the method of Rubingh and Yu.[18] All *trans*-decalin solutions and benzene were optically clarified by centrifugation.

The excess reduced intensity R_θ of unpolarized scattered light at scattering angle θ was obtained for vertically polarized incident light by subtracting the reduced intensity for the pure solvent from that for the solution. Optical anisotropy correction was necessary only for the lowest molecular weight sample A1000a and made according to the conventional method with ρ_u determined for both solution and solvent (see ref 8). The data of Kc/R_θ obtained were extrapolated to zero angle using Berry's plot[19] of $(Kc/R_\theta)^{1/2}$ vs $\sin^2(\theta/2)$, where K denotes the optical constant.

The specific refractive index increment $(\partial n/\partial c)$ for polystyrene in *trans*-decalin was determined at 21, 25, 35, and 45 °C for sample F-40B (at 546 nm) and at 21, 30, and 40 °C for the four lowest molecular weight samples (at 436 nm) in the c ranges studied for ρ. Use was made of a modified Schulz–Cantow type differential refractometer. The results for sample F-40B were found to be represented by

$$(\partial n/\partial c) = 1.50 \times 10^{-4}T + 0.1224 - 0.02c \quad (\text{at 546 nm and } c < 0.05 \text{ g cm}^{-3})$$

where $(\partial n/\partial c)$, T, and c are expressed in units of cm^3 g^{-1}, °C, and g cm^{-3}, respectively. This relation was used for the six higher molecular weight samples. The $(\partial n/\partial c)$ values obtained for the four lowest molecular weight samples were independent of c in the range studied but dependent on molecular weight. The results at 21, 30, and 40 °C were respectively 0.1353, 0.1366, and 0.1383 cm^3 g^{-1} for sample F-1b, 0.1349, 0.1363, and 0.1381 cm^3 g^{-1} for A5000b, 0.1279, 0.1292, and 0.1305 cm^3 g^{-1} for A2500b, and 0.1203, 0.1217, and 0.1235 cm^3 g^{-1} for A1000a. Necessary values at other temperatures were graphically interpolated or extrapolated.

Results and Discussion

Analysis of Scattering Intensity Data. Figure 1 illustrates the concentration dependence of Kc/R_0 for sample A5000b in *trans*-decalin at the indicated temperatures, where R_0 denotes the zero scattering angle value of R_θ. The curves fitting the data points at the respective T convex downward and converge to a common intercept.

These data were analyzed according to the equation[5]

$$\begin{aligned} S(c_1,c_2) &\equiv [(Kc/R_0)_{c=c_2} - (Kc/R_0)_{c=c_1}]/(c_2 - c_1) \\ &= 2A_2 + 3A_3(c_1 + c_2) + \ldots \end{aligned} \tag{15}$$

where c_1 and c_2 denote different c values. The plots of $S(c_1,c_2)$ vs $c_1 + c_2$ constructed are shown in Figure 2. The data points at any T follow a straight line throughout the entire concentration range examined, allowing unequivocal determination of A_2 and A_3. Table 1 presents the values of A_2 and A_3 thus obtained for all samples at 21 °C, the Θ temperature for polystyrene in *trans*-decalin (see below).

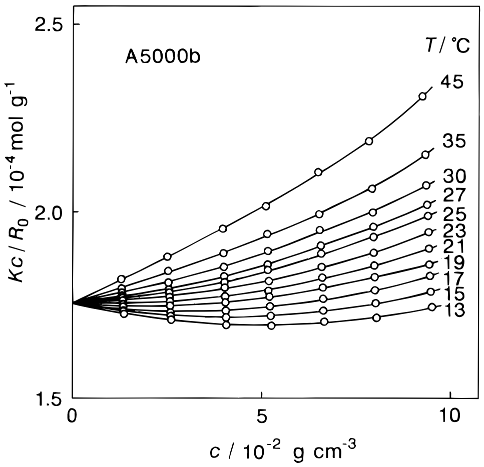

Figure 1. Concentration dependence of Kc/R_0 for polystyrene sample A5000b in *trans*-decalin at different temperatures.

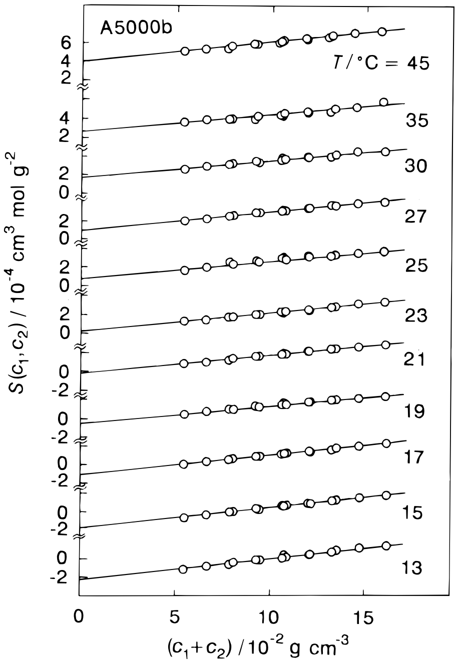

Figure 2. Plots of $S(c_1,c_2)$ vs $c_1 + c_2$ for polystyrene sample A5000b in *trans*-decalin at the indicated temperatures.

The weight-average molecular weight M_w of a given sample at each T was evaluated by extrapolation of its apparent value $[(Kc/R_0) - 2A_2c - 3A_3c^2]^{-1}$ to infinite dilution. The values of M_w thus obtained for the respective samples at different T agreed within ±1%. Their mean values are presented in the second column of Table 1. We note that those for the six higher molecular weight samples are also in good agreement with the previous results[2,20] in benzene and cyclohexane.

Second Virial Coefficient. All A_2 data are displayed as a plot against T for each sample in Figure 3a,b. The Θ point for the polystyrene + *trans*-decalin system is determined as 21 °C, since the A_2 values for the two highest molecular weight samples at the temperature are zero within experimental error (see also Table 1). This Θ temperature agrees with that reported by Konishi et al.,[21] who determined it using three samples with M_w of 3.7×10^5 to 1.3×10^6.

Table 1. Results from Light Scattering Measurements on Polystyrene Samples in *trans*-Decalin at the Θ Temperature

sample	$10^{-4}M_w$	10^4A_2, mol g^{-2} cm^3	10^4A_3, mol g^{-3} cm^6
F288-B	308	0.03[a]	9
F80-B	84.3	−0.02[a]	7
F-40B	37.2	−0.10	4.4
4a-B	9.62	−0.20	4.7
F'4-B	5.12	−0.16	3.3
2b-B	2.06	−0.30	5.0
F-1b	0.969	−0.40	7.6
A5000b	0.570	0.10	6.3
A2500b	0.267	0.25	9.1
A1000a	0.122	1.45	15.7

[a] Can be regarded as zero within experimental error.

Figure 4 shows plots of A_2 vs log M_w at several temperatures including Θ. As M_w decreases, the solid lines fitting the data points at the respective temperatures first rise (at $T \geq 30$ °C) or decline (at $T \leq 25$ °C) rather gradually and then sharply rise regardless of T. This sharp upswing of A_2 at low M_w may be ascribed to the effect of chain ends, as discussed in detail by Yamakawa and co-workers[9,10,17,22−24] for other polymer + solvent systems. The M_w dependence of $A_2(\Theta)$ observed here is similar to the behavior of a-PMMA in acetonitrile[10] but quite different from that of polystyrene in cyclohexane,[9,25] whose $A_2(\Theta)$ becomes positive at $M_w \sim 2 \times 10^4$ and monotonically increases with lowering M_w.

Yamakawa[17] evaluated the single-contact terms of the contribution $A_2^{(E)}$ from the chain ends to A_2 in the binary cluster approximation, with the result that

$$A_2^{(E)} = a_1 M^{-1} + a_2 M^{-2} \tag{16}$$

where a_1 is defined by

$$a_1 = 2N_A\beta_{2,1}/M_0 \tag{17}$$

and a_2 is a similar factor associated with the binary cluster integral for the interaction between the two end beads (see ref 17). Since A_2 for high M vanishes at Θ, eq 16 predicts that $A_2(\Theta)M_w$ should vary linearly with M_w^{-1}. We found, however, that such linearity approximately holds only for our $A_2(\Theta)$ data (at 21 °C) for $M_w < 6 \times 10^3$. The dashed line in Figure 4 represents the $A_2(\Theta)$ values calculated from eq 16 with $a_1 = -0.2$ cm^3 g^{-1} and $a_2 = 560$ cm^3 mol^{-1}. Its appreciable upward deviation from the data points in the molecular weight range between 1×10^4 and 1×10^5 indicates that a certain additional factor must be considered to explain the molecular weight dependence of experimental $A_2(\Theta)$. Residual ternary contributions at finite M as discussed previously[2,3] might be such a factor, but their consideration alone fails to explain $A_2(\Theta)$ in cyclohexane which begins to increase from zero (in contrast to the behavior in *trans*-decalin) when M_w decreases to 2×10^4. We wish to leave a consistent theoretical interpretation for future work.

Third Virial Coefficient. The temperature dependence of A_3 is displayed as a function of molecular weight in Figure 5a,b. The curves for the three highest molecular weight samples (Figure 5a) have a positive minimum around the Θ temperature (21 °C), rising with lowering T below Θ in contrast to the two-parameter theory prediction mentioned in the Introduction, while those for $M_w < 10^5$ are essentially horizontal (Figure 5a,b). These findings are similar to what we found previously for high molecular weight samples of polystyrene in cyclohexane[2] and polyisobutylene in isoamyl isovalerate[3] and may be explained qualitatively in terms of eq 2 with eqs 4 and 5 as follows.

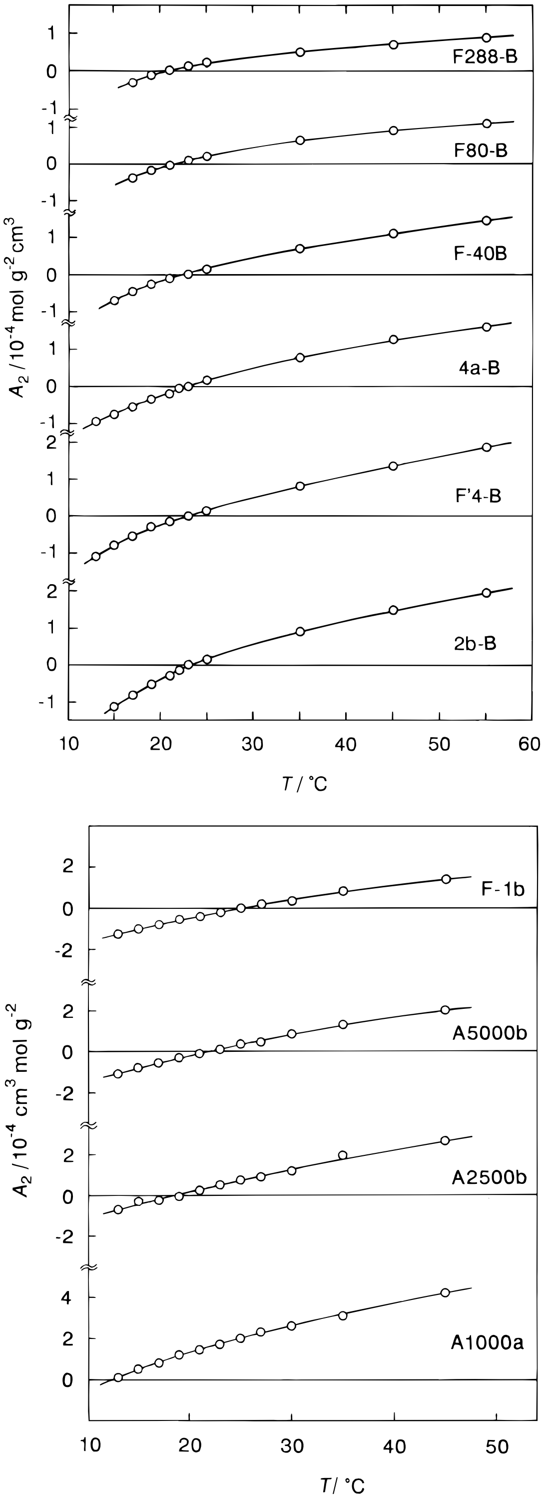

Figure 3. (a) Temperature dependence of A_2 for higher molecular weight polystyrene samples in *trans*-decalin (upper). (b) Temperature dependence of A_2 for lower molecular weight polystyrene samples in *trans*-decalin (lower).

As the A_2 data in Figure 3a show, z for the polystyrene + *trans*-decalin system is positive for $T > \Theta$ and negative for $T < \Theta$. If β_3 for the system, which is positive at the Θ point (see Figure 5a and eq 7), is insensitive to T, $\beta_3 H(z)$ is positive below Θ and a sharply decreasing function of T. On the other hand, the function $(2\pi b^2/3)^3 I(z)$ corresponding to the two-param-

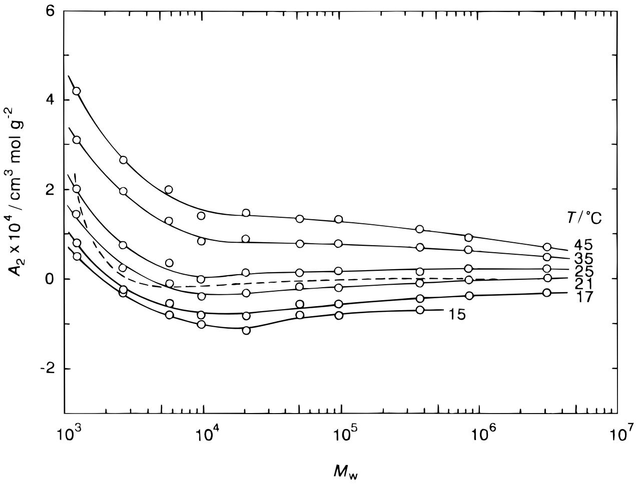

Figure 4. Molecular weight dependence of A_2 for polystyrene in *trans*-decalin at indicated temperatures. The dashed line represents the $A_2(\Theta)$ values calculated from eq 16 with $a_1 = -0.2$ cm^3 g^{-1} and $a_2 = 560$ cm^3 mol^{-1}.

eter theory is an increasing function of T. The sum of these two functions opposite with respect to a change in T should give A_3 a positive minimum somewhere around Θ (see ref 4 for a more quantitative discussion). For lower molecular weight samples, $|z|$ (or correctly $|\tilde{z}|$) stays small over the T range studied, so that the temperature dependence of A_3 is weak.

In Figure 5a or in Table 1, the values of $A_3(\Theta)$ for the two highest M_w's are appreciably larger than those for $M_w = 2 \times 10^4$ to 4×10^5. Similar trends were observed for polystyrene in different solvents.[2,7] Though they may indicate something more than experimental errors, we are unable to give a reasonable explanation for them. Another but more important point to note is that A_3 at any T increases with decreasing M_w below 1×10^4 and thus undergoes significant end effects (Figure 5b and Table 1). Yamakawa et al.[6] found similar end effects on $A_3(\Theta)$ for polystyrene in cyclohexane and a-PMMA in acetonitrile; the latter system exhibited a sharp drop of $A_3(\Theta)$ after the increase.

In sum, the present A_3 data for high molecular weights provide additional evidence for the breakdown of the binary cluster approximation to A_3 of linear flexible polymers near the Θ point and those for low molecular weights show significant end effects. These findings are in line with predictions from the current theories[4,6] that take account of ternary cluster interactions and end effects.

Ternary Cluster Integral. We analyze A_3 data for low molecular weights on the basis of eq 13. To estimate H in this equation, we calculated β from the A_2 data for sample F288-B and the $\langle S^2\rangle_0/M$ value[21] of 7.39×10^{-18} cm^2 for sufficiently high molecular weight polystyrene in *trans*-decalin, using Barrett's $h(z)$ function[26]

$$h(z) = (1 + 14.3z + 57.3z^2)^{-0.2} \qquad (T > \Theta) \quad (18)$$

for $T > \Theta$ and the double-contact approximation $h(z) = 1 - C_1 z$ for $T < \Theta$; according to recent experimental work,[22] the double-contact approximation rather well explains A_2 data below Θ. We also note that the molecular weight of sample F288-B is high enough to be free from the stiffness effect on $h(z)$.

The estimated z values were in the range between -0.0060 and $+0.0286$ for the three lowest molecular weight samples (A1000a, A2500b, and A5000b) in the temperature range from 17 to 35 °C. Our analysis of

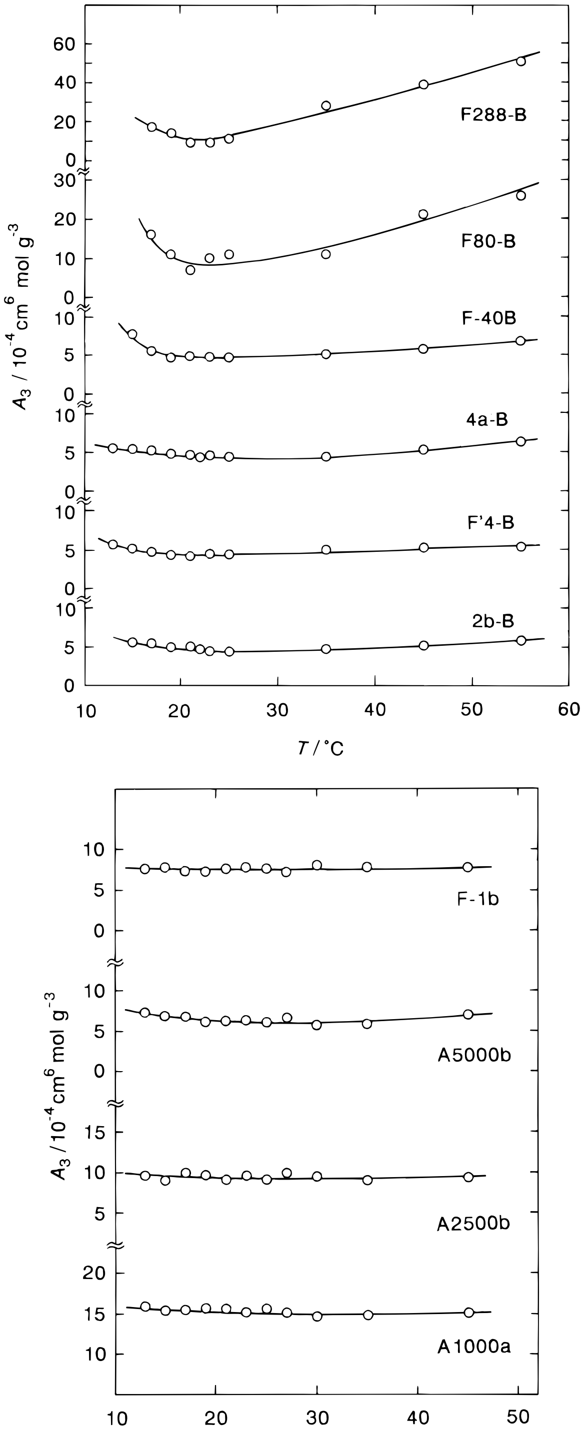

Figure 5. (a) Temperature dependence of A_3 for higher molecular weight polystyrene samples in *trans*-decalin (upper). (b) Temperature dependence of A_3 for lower molecular weight polystyrene samples in *trans*-decalin (lower).

A_3 data below is confined to these samples in this T range to diminish possible theoretical errors coming from the H function; note that for those z values, $I(z)$ in eq 2 can safely be ignored and the expansion factor for the radius of gyration can be set equal to unity. We converted z to $\tilde{z}$ with $\lambda^{-1} = 2.14$ nm and $M_L = 367$ nm^{-1} (at any T) for polystyrene in *trans*-decalin[21] and evaluated H by adopting eq 18 with $6\tilde{z}$ in place of z for $T > \Theta$ and the double-contact approximation $H = 1 - 6C_1 z$ (without stiffness effect[22]) for $T < \Theta$. The largest value of $\tilde{z}$ thus obtained was 0.019 for sample A5000b

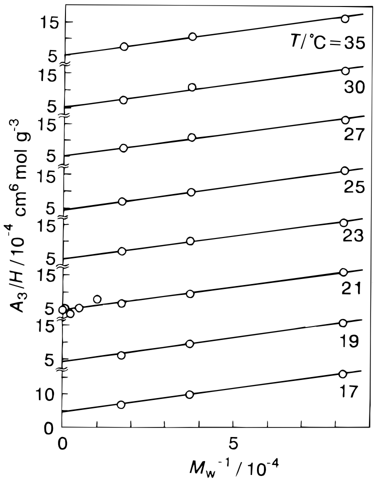

Figure 6. Plots of A_3/H vs M_w^{-1} for low molecular weight polystyrene samples in *trans*-decalin at indicated temperatures.

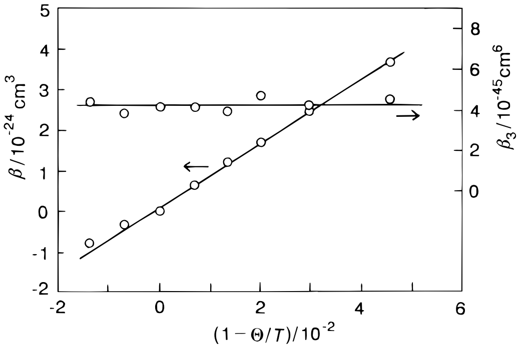

Figure 7. Temperature dependence of the effective binary cluster integral β and the ternary cluster integral β_3 for polystyrene in *trans*-decalin near the Θ temperature.

at 35 °C and the values of H were all within the range between 0.785 and 1.10.

Figure 6 shows the plots of A_3/H vs M_w^{-1} constructed for the three samples. The plot for $T = 21$ °C (the Θ temperature), where $\tilde{z} = 0$, includes data for several higher molecular weight samples. It is essentially linear and its intercept and slope yield $\beta_3 = 4.1 \times 10^{-45}$ cm^6 and $\beta_{3,1} = 2 \times 10^{-44}$ cm^6, respectively. These values are comparable to those ($\beta_3 = 4.4 \times 10^{-45}$ cm^6 and $\beta_{3,1} = 1.2 \times 10^{-44}$ cm^6) reported for polystyrene in cyclohexane at the Θ point.[6] We note that when the abscissa values (M_w^{-1}) were corrected for $H^{(E)}/H$ (see eq 13) with $\beta_{2,1} = -1.7 \times 10^{-23}$ cm^3 (obtained from $a_1 = -0.2$ cm^3 g^{-1}) and $\beta/\beta_{3,1} = 0.2$, the slope of the resulting plot and hence $\beta_{3,1}$ did not virtually alter.

The plotted points at the other temperatures in Figure 6 also follow respective straight lines, and the desired β_3 may be estimated from the intercepts. All the straight lines appear almost parallel with each other, indicating that $\beta_{3,1}$ at any T in the range studied is on the order of 2×10^{-44} cm^6.

The values of β_3 obtained are plotted against $(1 - \Theta/T)$ in Figure 7, along with those of β. While β increases almost linearly with $(1 - \Theta/T)$, β_3 stays essentially constant with a value of 4 (±0.5) × 10^{-45} cm^6 throughout the entire temperature range examined. In the polymer literature,[27] β_3 is often assumed to be independent of T by analogy with the weak T-dependence of the third virial coefficient for imperfect monatomic gases near the Boyle point. Our analysis demonstrates for the first time that this assumption essentially holds at least for the polystyrene + *trans*-decalin system near the Θ temperature.

Conclusions

The present A_3 data for polystyrene samples covering a broad range in M_w from 1.2×10^3 to 3.1×10^6 in *trans*-decalin give further evidence for the complete breakdown of the binary cluster approximation to A_3 near the Θ point and show significant end effects for M_w below 10^4. The ternary cluster integral for this system is 4(±0.5) × 10^{-45} cm^6, being essentially independent of temperature in the range examined (i.e., from 17 to 35 °C).

Acknowledgment. This work was supported by a Grant-in-Aid (06403027) for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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MA961222D