Second and Third Virial Coefficients of Polystyrene with Benzyl Ends near the Θ Point

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Received March 3, 2005

ABSTRACT: Second and third virial coefficients (A_2 and A_3, respectively) for cyclohexane solutions of linear polystyrene (benzyl-PS) samples, synthesized with benzyllithium (*n*-butyllithium/tetramethylethylenediamine/toluene ligand complex) as an initiator, were determined as functions of temperature and weight-average molecular weight M_w ranging from 710 to 7650. At the Θ temperature (34.5 °C), where $A_2 = 0$ for sufficiently high M_w, A_2 decreased with lowering M_w, in contrast to the sharp increase reported for low molecular weight polystyrene with a butyl group (butyl-PS) at one of the chain ends. This molecular weight dependence of negative A_2 for benzyl-PS was explained, without consideration of end effects, by the recent theory of Yamakawa and Yoshizaki for the helical wormlike chain with three-segment interactions, while the upswing of positive A_2 for butyl-PS was ascribed primarily to the butyl end effect that surpasses the ternary cluster effect. The A_3 values for both benzyl- and butyl-PS were positive and increased with decreasing M_w, showing significant end effects. The end effect in the former was larger than that in the latter, indicating that the three-segment interaction among a chain-end unit and two middle units for benzyl-PS is larger than that for butyl-PS.

Introduction

Dilute solution properties of linear flexible polymers are usually formulated on the binary cluster approximation,[1] in which interactions among polymer segments are represented by the binary cluster integral β_2. This approximation, however, may cease to be valid near and at the Θ temperature where the second virial coefficient A_2 for sufficiently high molecular weight vanishes. This was demonstrated by positive third virial coefficients A_3 at Θ,[2−10] which can be explained as due to repulsive three-segment interactions according to the first- or second-order perturbation theory for A_3.[11−13] If the ternary cluster integral β_3 representing such an interaction is incorporated into the first-order A_2 theory, the resulting A_2 at Θ decreases from zero with decreasing molecular weight, in contrast to the experimental finding[9,14−17] that for various polymer + Θ solvent systems A_2 monotonically increases or once becomes negative and abruptly increases with lowering weight-average molecular weight M_w. In most cases, such molecular weight dependence of A_2 was accounted for by the effect from chain ends[18] in the binary cluster approximation without direct evidence for the end effect. This interpretation may be reconciled with the measured positive A_3 at Θ if the end effect is overwhelmingly large to conceal the ternary cluster effect on A_2.

An exception was reported for low molecular weight polyethylene in deuterated biphenyl at Θ by Boothroyed et al.,[19] who observed A_2 behavior similar to what was predicted by the aforementioned perturbation theory[12] with β_2 and β_3. It is notable that the end groups of those samples were chemically similar to the middle chain groups. On the other hand, the polystyrene samples used for the previous A_2 studies[5,9,14,15] were synthesized by anionic polymerization with butyllithium as the initiator, so that the initiated end of each chain has a butyl group (Figure 1a). This chain end differing from the styrene residue may affect the virial coefficients of the polymer of low molecular weight. Using benzyllithium (*n*-butyllithium/tetramethylethylenediamine/toluene ligand complex) for the initiation of polymerization,[20] we may obtain polystyrene chains having at each initiated end a benzyl group (Figure 1b) whose chemical structure is the same as that of the terminated end and similar to that of the middle chain groups. The chain-end effect on A_2 for this polymer should be much smaller than those observed for polystyrene with the butyl group (butyl-PS).

In the present work, we prepared low molecular weight samples of polystyrene with benzyl ends (benzyl-PS) and determined A_2 and A_3 for those samples in cyclohexane at and near the Θ temperature by light scattering in expectation of observing the ternary cluster effect on A_2. The results are analyzed below in comparison with published A_2 and A_3 data[7,14,15] for butyl-PS in the same solvent to see effects of end groups. Another purpose of this study is to compare the present A_2 data with the recent theory of Yamakawa and Yoshizaki,[21] who investigated the effects of three-segment interaction and chain stiffness on A_2 for short helical wormlike chains.[22]

Experimental Section

Polymer Samples. Five benzyl-PS samples were synthesized by anionic polymerization of styrene with benzyllithium as an initiator. These samples except the lowest molecular weight one were fractionally precipitated with benzene as the solvent and methanol as the precipitant to remove high and low molecular weight components and were freeze-dried from benzene solutions. The lowest molecular weight sample was similarly fractionated, and the middle fraction was reprecipitated from an acetone solution into water and dried in a vacuum oven for 72 h at 80 °C. The five fractions thus prepared were designated as PS700, PS1900, PS3300, PS3400, and

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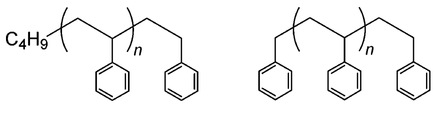
10.1021/ma0504567 CCC: $30.25



(a) butyl-PS (b) benzyl-PS

Figure 1. Chemical structures of butyl- and benzyl-end polystyrenes.

Table 1. Weight-Average Molecular Weights and Density and Refractive Index Increments for Benzyl-PS in Cyclohexane at 34.5 °C and 436 nm

sample	M_w	$\partial\rho/\partial c$	$\partial n/\partial c$
PS7700	7650	0.288_5	0.181_6
PS3400	3440		0.181_6
PS3300	3320	0.284_8	
PS1900	1870	0.283_1	0.180_9
PS700	710	$(0.281_0)^a$	$(0.175_1)^a$

[a] Values at 35 °C.

PS7700 in the order of increasing molecular weight. We confirmed their initiated ends to be benzyl by ^{1}H NMR.

Ratios of the weight- to number-average molecular weight M_w/M_n for PS700, PS1900, PS3400, and PS7700 were estimated to be 1.13, 1.06, 1.03, and 1.01, respectively, by matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (Shimadzu-Kratos Kompact IV), while that for PS3300 was estimated to be 1.08 by gel permeation chromatography.

Preparation of Solutions. Cyclohexane was refluxed over sodium for 5 h and then fractionally distilled. Each polymer sample was mixed with the solvent under stirring overnight at room temperature. The polymer mass concentration c in units of g cm^{-3} was calculated from the gravimetrically determined polymer weight fraction with the solution density ρ, which was determined by use of an Anton-Paar densitometer at 25, 30, 35, 40, and 45 °C for PS7700, PS3300, and PS1900 and at 25, 35, and 45 °C for PS700.

Light Scattering. Scattering intensities were measured for PS1900, PS3300, PS3400, and PS7700 in cyclohexane at different temperatures T between 25 and 42 °C on a Fica-50 light scattering photometer in an angular range from 30° to 150°. Vertically polarized incident light of 436 nm wavelength was used. The apparatus was calibrated with benzene at 25 °C with the Rayleigh ratio for the unpolarized light at 90° taken as 46.5×10^{-6} cm^{-1}.[23] The depolarized ratio ρ_u of this liquid was determined to be 0.42 by the method of Rubingh and Yu.[24] Test solutions were optically clarified by filtration through Millipore filters with 0.2 μm pore size.

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, necessary for PS1900, was made according to the conventional method with ρ_u determined for both solution and solvent (see ref 25). The data of Kc/R_θ obtained were extrapolated to zero angle using the $(Kc/R_\theta)^{1/2}$ vs $\sin^2(\theta/2)$ plot[26] (though they were essentially independent of θ), where K denotes the optical constant.

The specific refractive index increment $\partial n/\partial c$ at 436 nm for benzyl-PS in cyclohexane was determined at 25, 30, 35, 40, and 45 °C for PS1900 and PS7700, at 25, 30, 40, and 50 °C for PS3400, and at 35 °C for PS700. The value at 546 nm was also measured for the last sample. Use was made of a modified Schulz–Cantow type differential refractometer.

The values of M_w, $\partial\rho/\partial c$, and $\partial n/\partial c$ at 436 nm for benzyl-PS samples in cyclohexane at 34.5 °C (the interpolated values except M_w) are summarized in Table 1. Both $\partial\rho/\partial c$ and $\partial n/\partial c$ are seen to be dependent weakly on molecular weight. For PS3400, we used the $\partial\rho/\partial c$ and $\partial n/\partial c$ values for PS3300 since the molecular weights of the two samples are quite close to each other.

Sedimentation Equilibrium. Sedimentation equilibrium measurements were made on six cyclohexane solutions of PS700 with different concentrations at a rotor speed of 10 000 rpm in a Beckman Optima XL-1 ultracentrifuge at 35 °C. The concentration profile of each solution in a 12 mm aluminum double-sector cell was monitored by the Rayleigh interference detector with a diode laser of 675 nm wavelength. The value of $\partial n/\partial c$ at this wavelength (λ_0) was obtained by extrapolation of the measured values at 436 and 546 nm using a plot of $\partial n/\partial c$ against λ_0^{-2} based on the Cauchy relation. The solution column height was adjusted to 2.5 mm. From the polymer mass concentrations at the meniscus and the cell bottom, c_a and c_b, respectively, the apparent molecular weight M_{app} defined by

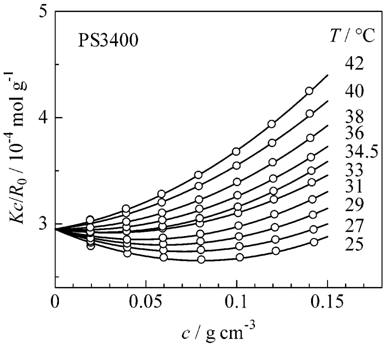


Figure 2. Plots of Kc/R_0 against c for benzyl-end polystyrene sample PS3400 in cyclohexane at the indicated temperatures.

$$M_{app} = \frac{2RT(c_b - c_a)}{\omega^2({r_b}^2 - {r_a}^2)(d\rho/dc)c_0} \tag{1}$$

was calculated, where r_a and r_b are the distances from the center of revolution to the meniscus and the bottom, respectively, ω is the angular velocity, c_0 is the polymer mass concentration before centrifugation, and R is the gas constant. The apparent molecular weight for a narrow-distribution sample is expressed by[27]

$$M_{app}^{-1} = M_w^{-1} + 2A_2\bar{c} + 3A_3\bar{c}^2\left[1 + \frac{1}{12}\left(\frac{c_b - c_a}{\bar{c}}\right)^2\right] + ... \tag{2}$$

with

$$\bar{c} = (c_a + c_b)/2 \tag{3}$$

Results

Figure 2 illustrates the concentration dependence of Kc/R_0 for benzyl-end polystyrene sample PS3400 in cyclohexane at the indicated temperatures, where R_0 denotes the zero-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[28,29]

$$S(c_i,c_j) \equiv \frac{(Kc/R_0)_{c=c_j} - (Kc/R_0)_{c=c_i}}{c_j - c_i} = 2A_2 + 3A_3(c_i + c_j) + ... \tag{4}$$

where c_i and c_j denote different c values. The plots of $S(c_i,c_j)$ vs $(c_i + c_j)$ constructed are shown in Figure 3, where the data for pairs of neighboring c_i and c_j in a series of polymer concentrations are omitted since they were less accurate. 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. Similar plots for different samples at 34.5 °C are presented in Figure 4, which includes the sedimentation

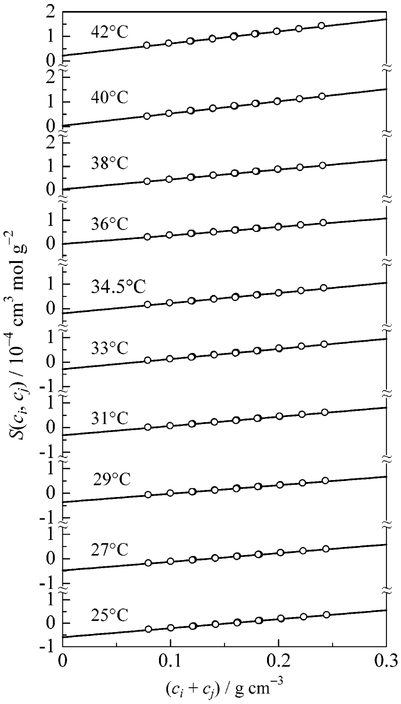


Figure 3. Bawn plots for sample PS3400 at the indicated temperatures.

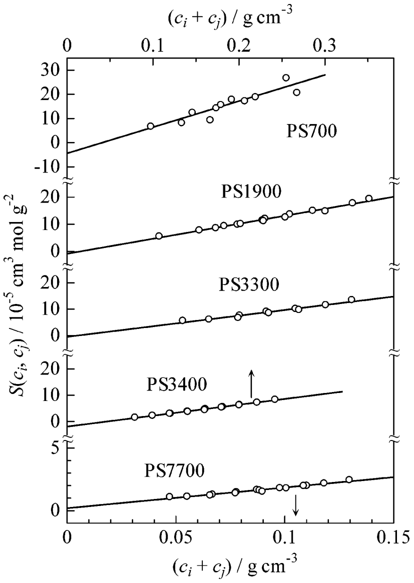


Figure 4. Bawn plots for benzyl-PS samples in cyclohexane at 34.5 °C.

equilibrium data for PS700 analyzed according to

$$S(\bar{c}_i,\bar{c}_j) \equiv \frac{({M_{\mathrm{app}}}^{-1})_{\bar{c}=\bar{c}_j} - ({M_{\mathrm{app}}}^{-1})_{\bar{c}=\bar{c}_i}}{\bar{c}_j - \bar{c}_i} = 2A_2 + 3A_3(\bar{c}_i + \bar{c}_j) + \ldots \tag{5}$$

(for simplicity, $S(\bar{c}_i,\bar{c}_j)$, $\bar{c}_i$, and $\bar{c}_j$ are denoted as $S(c_i,c_j)$, c_i, and c_j, respectively, in the figure). The second term in the square bracket in eq 2, ignored in eq 5, did not affect the estimation of A_3 in our low-speed experiment.

The weight-average molecular weight of a given sample at each T was evaluated by extrapolation of $[(Kc/R_0) - 2A_2c - 3A_3c^2]^{-1}$ to infinite dilution. The values of M_w thus obtained for each sample at different temperatures agreed within ±3%.

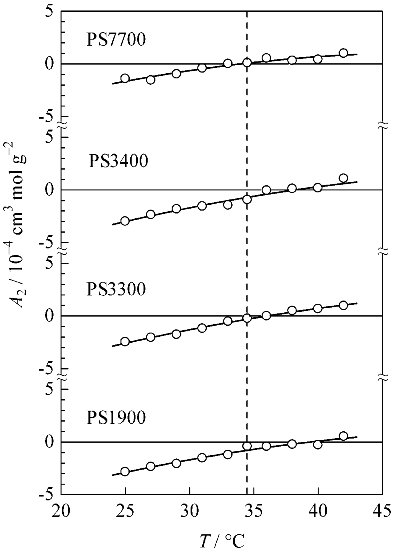


Figure 5. Temperature dependence of second virial coefficient for the indicated benzyl-PS samples. The vertical dashed line indicates the Θ temperature.

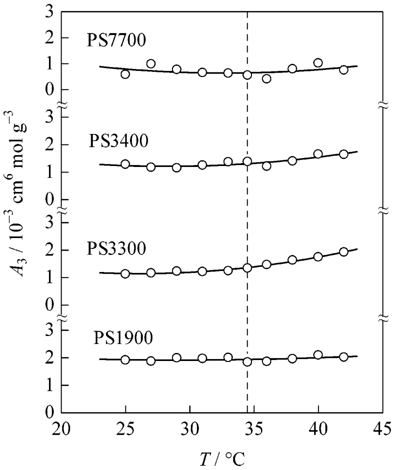


Figure 6. Temperature dependence of third virial coefficient for the indicated benzyl-PS samples. The vertical dashed line indicates the Θ temperature.

Figures 5 and 6 illustrate the temperature dependence of A_2 and A_3, respectively, where the vertical dashed lines indicate the Θ point (34.5 °C) at which $A_2 = 0$ for high M_w ($>5 \times 10^4$).[5] In the former, each A_2 curve rises with increasing T in the fashion commonly observed for linear flexible polymers near the Θ point. In the latter, A_3 for any sample has a very weak temperature dependence (see ref 13 for theoretical explanation and discussion). Its positive values confirm that the binary cluster approximation to A_3 at and near Θ breaks down. The numerical results for A_2 and A_3 are summarized in Tables 2 and 3, respectively. It should be noted in the latter table that, as M_w increases, A_3 at 34.5 °C decreases toward the value (0.4−0.5) × 10^{-3} cm^6 mol g^{-3} established previously for high molecular weight butyl-PS.[5]

Discussion

Second Virial Coefficient. Figure 7 shows a marked contrast between A_2 for low molecular weight benzyl-PS (unfilled circles) and that for butyl-PS[15] (filled circles), both in cyclohexane at 34.5 °C. Namely, the former is negative and decreases with decreasing mo-

Table 2. Second Virial Coefficients for Benzyl-PS in Cyclohexane at Different Temperatures

	$A_2/10^{-4}$ cm^3 mol g^{-2}				
T/°C	PS700	PS1900	PS3300	PS3400	PS7700
25		−2.84	−2.47	−2.98	−1.40
27		−2.35	−2.05	−2.36	−1.55
29		−2.06	−1.76	−1.82	−0.97
31		−1.53	−1.19	−1.55	−0.42
33		−1.22	−0.53	−1.45	0
34.5	(−2.2)[a]	−0.42	−0.24	−0.94	0.10
36		−0.43	0	−0.05	0.53
38		−0.23	0.49	0.12	0.31
40		−0.28	0.69	0.18	0.42
42		0.53	0.97	1.09	0.99

[a] Value at 35 °C.

Table 3. Third Virial Coefficients for Benzyl-PS in Cyclohexane at Different Temperatures

	$A_3/10^{-3}$ cm^6 mol g^{-3}				
T/°C	PS700	PS1900	PS3300	PS3400	PS7700
25		1.9_1	1.1_3	1.2_8	0.5_8
27		1.8_7	1.1_6	1.1_7	0.9_9
29		1.9_9	1.2_3	1.1_5	0.7_7
31		1.9_7	1.2_1	1.2_5	0.6_5
33		2.0_0	1.2_4	1.3_7	0.6_3
34.5	(3.6)[a]	1.8_4	1.3_4	1.3_8	0.5_5
36		1.8_6	1.4_6	1.2_1	0.41
38		1.9_6	1.6_3	1.4_0	0.7_9
40		2.0_9	1.7_4	1.6_5	1.0_1
42		2.0_1	1.9_2	1.6_4	0.7_5

[a] Value at 35 °C.

lecular weight, while the latter is positive and increases sharply with decreasing M_w. This demonstrates for the first time that A_2 for short chains near Θ is strongly affected by chain end groups.

The dot−dashed line in Figure 7 represents the A_2 values calculated from[18]

$$A_2 = A_2^{(E)} \equiv a_1 M^{-1} + a_2 M^{-2} \tag{6}$$

for the end effects (at the Θ point) using $a_1 = 0.19$ and $a_2 = 270$ (both in units of cm^3 mol g^{-2}),[15] where the constant a_1 is associated with the interaction between a bead at one end of either of the two chains with molecular weight M and a middle bead in the other chain and the constant a_2, with the interactions between a pair of end beads belonging to different chains. The close fit of this line to the filled circles substantiates that the positive A_2 values and their remarkable increase (with lowering M_w) for butyl-PS at the Θ temperature are due primarily to the end effects. The ternary cluster effect on A_2 for this polystyrene is little significant as discussed at the end of this subsection.

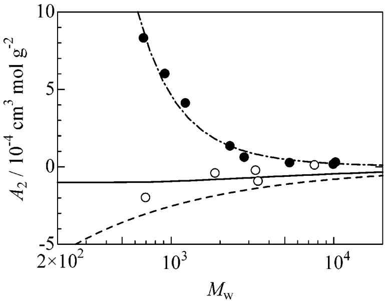


Figure 7. Molecular weight dependence of second virial coefficient for benzyl-PS (unfilled circles) and butyl-PS (filled circles)[15] in cyclohexane at 34.5 °C. The dot−dashed, dashed, and solid lines represent the theoretical values calculated from eqs 6, 9, and 10, respectively (see the text for the parameters used).

We analyze the data for benzyl-PS in terms of the ternary cluster effect because, as mentioned in the Introduction, the end effect should be small for the polymer. The first-order perturbation theory for A_2 of linear flexible chains with β_3 (based on the Gaussian chain model) is written[12]

$$A_2 = \frac{N_A n^2}{2M^2}\left[\beta_2 + \frac{4}{\sqrt{\sigma}}\left(\frac{3}{2\pi b^2}\right)^{3/2}\left(1 - 2\sqrt{\frac{\sigma}{n}}\right)\beta_3\right] \tag{7}$$

Here, N_A is the Avogadro constant, n the number of beads in a chain, b the bond length, and σ a cutoff parameter representing the minimum number of consecutive beads necessary for the formation of a loop within one chain. According to eq 7, the Θ condition ($A_2 = 0$ for high M) satisfies the relation

$$\beta_2 + C\beta_3 = 0 \tag{8}$$

with $C = (4/\sigma^{1/2})(3/2\pi b^2)^{3/2}$, and A_2 at Θ is given by

$$A_2 = -\frac{4N_A}{\sqrt{n}}\left(\frac{n}{M}\right)^2\left(\frac{3}{2\pi b^2}\right)^{3/2}\beta_3 \tag{9}$$

This equation predicts A_2 to be negative and decrease with decreasing n or M.

The dashed line in Figure 7 represents the A_2 values calculated from eq 9 with $\beta_3 = 4 \times 10^{-3}$ nm^6 (from A_3 data for high M_w at Θ),[5] $M/n = 104$, and $b = 0.74$ nm (from $\langle S^2\rangle/M_w$ for polystyrene in cyclohexane[30] at Θ). This curve deviates downward significantly from the unfilled circles.

Yamakawa and Yoshizaki[21] calculated the first-order β_3 term of A_2 for the helical wormlike bead chain. Their equation in the wormlike chain limit at Θ reads

$$A_2 = -\frac{N_A \lambda^2 L^2}{M^2}\left(\frac{3}{2\pi a^2}\right)^{3/2}\beta_3[I(\infty) - I(\lambda L)] \tag{10}$$

Here, L is the contour length of the chain, a is the bead spacing, λ^{-1} is the stiffness parameter or the Kuhn segment length, and $I(\lambda L)$ is a known function of λL (eq 36 of ref 21); for the wormlike chain, C in eq 8 is given by $2.93(3/2\pi a^2)^{3/2}(\lambda a)^2$.

In Figure 7, the solid line calculated from eq 10 with $\lambda^{-1} = 2$ nm and M_L $(= M/L) = 390$ nm^{-1} (the molar mass per unit contour length)[31] comes close to the unfilled circles. Thus, we may conclude that the effects of chain stiffness and three-segment interaction are essential to explain A_2 for benzyl-PS of low molecular weight at Θ and that the chain end effect is negligibly small or, at least, need not be considered. As the molecular weight decreases, the solid curve appears to begin deviating from zero at a higher molecular weight than do the unfilled circles, but the present data are not extensive enough to discuss the accuracy of the Yamakawa−Yoshizaki theory. Boothroyed et al.[19] estimated β_3 for polyethylene in deuterated biphenyl using eq 7 for ideally flexible chains. Their β_3 must be considerably underestimated because this equation gives much smaller A_2 (see the large difference between the solid and dashed lines in Figure 7).

As can be seen from the above analysis, the ternary cluster effect on A_2 of polystyrene is rather small. If this

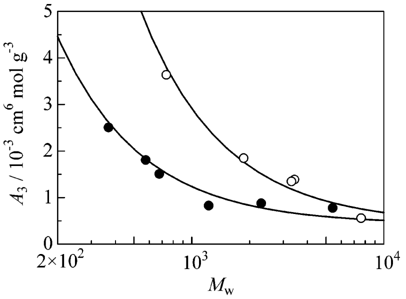


Figure 8. Molecular weight dependence of third virial coefficient for benzyl-PS (unfilled circles) and butyl-PS (filled circles)[7] in cyclohexane at 34.5 °C. The solid lines represent the theoretical values calculated from eq 12 with eqs 11 and 13 (see the text for the parameters used).

effect is taken into consideration in the data analysis for A_2 of butyl-PS, the values of a_1 and a_2 in eq 6 become only slightly larger without impairing the close fit of the dot−dashed line to the filled circles.[21] In short, the ternary cluster and end effects are responsible primarily for the decline and upswing of A_2, respectively, with a decrease in M_w. If the latter effect is smaller than what was observed for cyclohexane solutions, A_2 may first decrease below zero and rise beyond zero with lowering M_w. Such behavior was indeed observed for butyl-PS in *trans*-decalin.[9]

Third Virial Coefficient. Figure 8 shows the molecular weight dependence of A_3 for benzyl-PS and butyl-PS[7] in cyclohexane at Θ. For both polymers, A_3 increases with lowering M_w, but interestingly, the values for benzyl-PS are systematically larger than those for butyl-PS.

The third virial coefficient A_3^0 for long flexible chains with ternary cluster interactions at Θ may be written[11−13]

$$A_3^0 = \frac{{N_A}^2 n^3}{3M^3}\beta_3 \tag{11}$$

which predicts that A_3 at Θ is positive (for a positive β_3) and independent of molecular weight unless M is low. This is consistent with A_3 data for polystyrene of high molecular weight ($M_w > 1 \times 10^4$).[5] If the chain end effect is taken into account, A_3 at Θ may be written as[7]

$$A_3 = A_3^0 + {A_3}^{(E)} \tag{12}$$

with

$${A_3}^{(E)} = \frac{2{N_A}^2}{n}\left(\frac{n}{M}\right)^3\beta_{001} \tag{13}$$

up to the order of n^{-1}, where β_{001} denotes the ternary cluster integral concerning the interaction among one end and two middle beads. We note that, if the end groups of the polymer are different as is the case with butyl-PS, β_{001} is the mean of the two contributions.

The solid lines in Figure 8 represent the theoretical values calculated from eq 12 with eqs 11 and 13 using $\beta_3 = 4 \times 10^{-3}$ nm^6, $\beta_{001} = 0.037$ nm^6 for benzyl-PS, and $\beta_{001} = 0.012$ nm^6 for butyl-PS.[7] They come quite close to the data points for the respective polymers, showing that the effects from chain ends are essential to explain A_3 for low molecular weight polystyrene in cyclohexane at Θ. The input value of β_{001} for benzyl-PS is larger than that for butyl-PS though the binary cluster integrals (or a_1 and a_2 in eq 6) associated with the benzyl ends are negligibly small. This seemingly contradictory finding is consistent with the theoretical fact[32] that the third virial coefficient for monatomic gas molecules at or slightly below the Boyle point (where the second virial coefficient B_2 for the gas molecules is zero or negative) can be larger than those in a certain temperature range above the Boyle point (where $B_2 > 0$).

Conclusions

The second virial coefficient for benzyl-end polystyrene of low molecular weight ($700 < M_w < 7700$) in cyclohexane at Θ is negative and decreases with lowering M_w, in contrast to the sharp increase reported for butyl-end polystyrene,[14,15] in the same solvent. This demonstrates for the first time that the chain-end groups strongly affect A_2 for low molar mass polystyrene. The M_w dependence of A_2 for benzyl-PS is explained by the recent theory of Yamakawa and Yoshizaki[21] as due to the effects of chain stiffness and ternary cluster interaction, the effects of the benzyl ends being negligibly small. On the other hand, the sharp increase for butyl-end polystyrene is attributable primarily to the butyl-end effect, which surpasses the effects of chain stiffness and three-segment interaction. The end effect on A_3 at Θ is significant for the two polystyrenes in cyclohexane, and interestingly, it is stronger for benzyl-end polystyrene.

Acknowledgment. We thank Professor Takenao Yoshizaki of Kyoto University for valuable discussions and Manabu Sugiyama of our group for his help in the preparation of some of the polystyrene samples used in this study.

References and Notes

(1) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(2) Vink, H. *Eur. Polym. J.* **1974**, *10*, 149.
(3) Murakami, H.; Norisuye, T.; Fujita, H. *Polym. J.* **1975**, *7*, 248.
(4) Chen, S.-J.; Berry, G. C. *Polymer* **1990**, *31*, 793.
(5) Nakamura, Y.; Norisuye, T.; Teramoto, A. *Macromolecules* **1991**, *24*, 4904.
(6) Akasaka, K.; Nakamura, Y.; Norisuye, T.; Teramoto, A. *Polym. J.* **1994**, *26*, 363.
(7) Yamakawa, H.; Abe, F.; Einaga, Y. *Macromolecules* **1994**, *27*, 3272.
(8) Li, J.; Wan, Y.; Xu, Z.; Mays, J. W. *Macromolecules* **1995**, *28*, 5347.
(9) Nakamura, Y.; Inoue, N.; Norisuye, T.; Teramoto, A. *Macromolecules* **1997**, *30*, 631.
(10) Osa, M.; Yoshizaki, T.; Yamakawa, H. *Polym. J.* **2004**, *36*, 634.
(11) Zimm, B. H. *J. Chem. Phys.* **1946**, *14*, 164.
(12) Cherayil, B. J.; Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1985**, *83*, 5293.
(13) Norisuye, T.; Nakamura, Y. *Macromolecules* **1994**, *27*, 2054.
(14) Huber, K.; Stockmayer, W. H. *Macromolecules* **1987**, *20*, 1400.
(15) Einaga, Y.; Abe, F.; Yamakawa, H. *Macromolecules* **1993**, *26*, 6243.
(16) Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1995**, *28*, 694.
(17) Tokuhara, W.; Osa, M.; Yoshizaki, T.; Yamakawa, H. *Macromolecules* **2003**, *36*, 5311.
(18) Yamakawa, H. *Macromolecules* **1992**, *25*, 1912.
(19) Boothroyd, A. T.; Rennie, A. R.; Boothroyd, C. B.; Fetters, L. J. *Phys. Rev. Lett.* **1992**, *69*, 426.
(20) Tsukahara, Y.; Inoue, J.; Ohta, Y.; Kohjiya, S.; Okamoto, Y. *Polym. J.* **1994**, *26*, 1013.
(21) Yamakawa, H.; Yoshizaki, T. *J. Chem. Phys.* **2003**, *119*, 1257.
(22) Yamakawa, H. *Helical Wormlike Chains in Polymer Solutions*; Springer: Berlin, 1997.
(23) Deželić, Gj.; Vavra, J. *Croat. Chem. Acta* **1966**, *38*, 35.
(24) Rubingh, D. N.; Yu, H. *Macromolecules* **1976**, *9*, 681.

(25) Einaga, Y.; Abe, F.; Yamakawa, H. *J. Phys. Chem.* **1992**, *96*, 3948.
(26) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.
(27) Fujita, H. *Foundations of Ultracentrifugal Analysis*; Wiley-Interscience: New York, 1975.
(28) Bawn, C. E. H.; Freeman, F. J.; Kamaliddin, A. R. *Trans. Faraday Soc.* **1950**, *46*, 862.
(29) Sato, T.; Norisuye, T.; Fujita, H. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1.
(30) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(31) Norisuye, T.; Fujita, H. *Polym. J.* **1982**, *14*, 143.
(32) Kihara, T. *Intermolecular Forces* (Translated by S. Ichimaru); John Wiley & Sons: New York, 1978.

MA0504567