

## Some Comments on the Analysis of the Third Virial Coefficient for Polymer Chains

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**ABSTRACT:** An analysis is made of experimental data for the third virial coefficient  $A_3$  of atactic oligo- and poly( $\alpha$ -methylstyrene)s (a-P $\alpha$ MS) in the  $\Theta$  solvent cyclohexane at 30.5 °C and in three good solvents, toluene, 4-*tert*-butyltoluene, and *n*-butyl chloride, at 25.0 °C on the basis of the helical wormlike (HW) chain model. It is found that  $A_3$  at  $\Theta$ , which is denoted by  $A_{3,\Theta}$ , becomes a constant of  $5.0 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$  independent of the weight-average molecular weight  $M_w$  for  $M_w \gtrsim 10^4$  and deviates from it for  $M_w \lesssim 10^4$  because of effects of chain ends. The observed dependence of  $A_{3,\Theta}$  on  $M_w$  may be well explained by the HW theory that takes account of the effects. For the three good-solvent systems, the behavior of the factor  $g$  defined by  $A_3/[A_2^{(\text{HW})}]^2 M_w$  is examined as a function of the cubed gyration-radius expansion factor  $\alpha_S^3$ , where  $A_2^{(\text{HW})}$  is the part of the second virial coefficient  $A_2$  without the effects of chain ends. It is found that the data points for a-P $\alpha$ MS samples with  $M_w \gtrsim 10^5$  in all the three good solvents form nearly a single-composite curve, as predicted by the HW theory, and that they follow the Stockmayer–Casassa theoretical curve for  $\alpha_S^3 \gtrsim 2$  but deviate upward from it for  $\alpha_S^3 \lesssim 2$  because of effects of three-segment interactions. Effects of chain stiffness are of minor importance for an explanation of this deviation. Some literature data for polystyrene are also examined. [DOI 10.1295/polymj.36.634]

**KEY WORDS** Third Virial Coefficient / Excluded-volume Effect / Chain Stiffness / Three-segment Interactions / Effect of Chain Ends / Helical Wormlike Chain / Poly( $\alpha$ -methylstyrene) / Polystyrene /

In our experimental studies of the intermolecular excluded-volume effect in dilute solutions of flexible polymers made so far within the new framework based on the helical wormlike (HW) chain model,<sup>1,2</sup> it has been shown for atactic polystyrene (a-PS),<sup>1–4</sup> atactic (a-) and isotactic poly(methyl methacrylate)s (PMMA),<sup>1,2,5,6</sup> and atactic poly( $\alpha$ -methylstyrene) (a-P $\alpha$ MS)<sup>7</sup> that for good-solvent systems the behavior of the second virial coefficient  $A_2$  as a function of the weight-average molecular weight  $M_w$  or of the interpenetration function  $\Psi$  appearing in it as a function of the cubed gyration-radius expansion factor  $\alpha_S^3$  may be well explained by the HW theory<sup>1,8</sup> that takes account of effects of chain stiffness and chain ends. It has also been shown that the behavior of  $A_2$  as a function of  $M_w$  for a-PS, a-PMMA, and a-P $\alpha$ MS in the respective  $\Theta$  solvents may be well explained by the HW theory at the  $\Theta$  temperature<sup>9</sup> with consideration of effects of chain ends and also three-segment interactions.

The third virial coefficient  $A_3$  is another important quantity which is concerned with the intermolecular excluded-volume effect in dilute polymer solutions. There has recently been substantial progress in an understanding of the behavior of  $A_3$  for flexible polymers on both experimental and theoretical sides. On the experimental side, it has been demonstrated by

Norisuye and co-workers<sup>10–16</sup> that  $A_2$  and  $A_3$  can be simultaneously determined rather unambiguously from light-scattering (LS) data by an application of the Bawn plot.<sup>17</sup> From the data so obtained for PS and polyisobutylene, they have derived the conclusions that  $A_3$  remains positive finite at the  $\Theta$  temperature, as already shown in earlier experimental studies,<sup>18–21</sup> and that for good-solvent systems the factor  $g$  defined by  $A_3/A_2^2 M_w$  as a function of  $\alpha_S^3$  is nearly consistent with the Stockmayer–Casassa (SC) theory prediction<sup>22,23</sup> for  $\alpha_S^3 \gtrsim 2$ . Subsequently, Li *et al.*<sup>24</sup> have obtained similar experimental results for PS in the  $\Theta$  and good solvents. On the theoretical side, the effects of chain ends on  $A_3$  have been formulated and analyzed for a-PS and a-PMMA in the respective  $\Theta$  solvents.<sup>25</sup> As for good-solvent systems, Norisuye *et al.*<sup>26</sup> have developed a theory of  $A_3$  with consideration of the effects of chain stiffness and three-segment interactions and claimed that the upward deviation of experimental data points from the SC theoretical curve in the plot of  $g$  vs.  $\alpha_S^3$  for  $\alpha_S^3 \lesssim 2$  arises from those effects. In the present paper, we make an analysis of  $A_3$  data obtained from previous LS measurements for a-P $\alpha$ MS<sup>7,27–29</sup> to examine the effects of chain ends on  $A_3$  at  $\Theta$  and reconsider Norisuye *et al.*'s conclusion for  $g$  for good-solvent systems. Some literature data for a-PS<sup>11,12</sup> are also used.

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In anticipation of analysis, it is pertinent to make here a short comment on the above-mentioned theory of Norisuye *et al.*<sup>26</sup> They have derived an approximate closed expression for the part of  $g$  involving the *effective* binary-cluster integral  $\beta$  on the basis of the SC theory values<sup>22</sup> with the use of a scaled excluded-volume parameter  $\check{z}$  newly introduced on the apparent analogy of the intra- and intermolecular scaled excluded-volume parameters<sup>1,2</sup>  $\tilde{z}$  and  $\tilde{\tilde{z}}$ . Strictly, however, the scale factor in their  $\tilde{z}$  arises from the leading (zeroth-order) term in the perturbation expansion of  $A_3$  (or  $g$ ) in contrast to those in  $\tilde{z}$  and  $\tilde{\tilde{z}}$  which arise from the first-order perturbation terms of  $\alpha_S^2$  and  $A_2$ , respectively. Thus their analogy is not self-consistent.

## RESULTS FOR a-P $\alpha$ MS

The values of  $A_3$  for 22 a-P $\alpha$ MS samples with  $M_w$  ranging from  $5.30 \times 10^2$  to  $5.46 \times 10^6$  in cyclohexane at 30.5 °C ( $\Theta$ ), those for 17 samples with  $M_w$  from  $6.48 \times 10^2$  to  $5.46 \times 10^6$  in toluene at 25.0 °C, and those for 6 samples with  $M_w$  from  $2.38 \times 10^5$  to  $5.46 \times 10^6$  in 4-*tert*-butyltoluene and *n*-butyl chloride at 25.0 °C had been determined from the Bawn plots<sup>17</sup> simultaneously in the previous<sup>7,29</sup> studies of  $A_2$ . The values of  $A_3$  so determined for a-P $\alpha$ MS in cyclohexane at  $\Theta$ , which we denote by  $A_{3,\Theta}$ , are given in Table I along with those of  $M_w$  which have been reproduced from refs 7 and 29. In Table II are given the values of  $A_3$  for a-P $\alpha$ MS in toluene, 4-*tert*-butyltoluene, and *n*-butyl chloride at 25.0 °C along with those of  $\alpha_S^3$ , where the values of  $\alpha_S^3$  for OAMS5, OAMS8, and OAMS10 have been assumed to be 1 as in ref 7, and those for OAMS13 through AMS550 have been reproduced from refs 7 and 28.

It is seen from Table I that the values of  $A_{3,\Theta}$  for a-P $\alpha$ MS in cyclohexane at 30.5 °C are positive and almost independent of  $M_w$  for  $M_w \gtrsim 10^4$ . From a com-

parison between the values of  $A_3$  for each of the samples AMS24 through AMS550 in different solvents given in Table II, it is seen that  $A_3$  increases with increasing solvent power ( $\alpha_S^3$ ).

## ANALYSIS AND DISCUSSION

### Basic Equations

In this subsection, we summarize basic equations in the HW and related theories necessary for an analysis of the experimental data for  $A_3$  in the  $\Theta$  and good solvents given in the last section.

The HW bead model (with excluded volume)<sup>1,25</sup> is such that  $n + 1$  beads are arrayed with spacing  $a$  between them along the contour of total length  $L = na$ , where  $n - 1$  intermediate beads are identical and the two end beads are different from the intermediate ones and also from each other in species. Identical excluded-volume interactions between intermediate beads are expressed in terms of the effective binary-cluster integral  $\beta$  and the ternary-cluster integral  $\beta_3$ . We note that  $\beta$  is defined by  $\beta = \beta_2 + \text{const.}\beta_3$  with  $\beta_2$  the conventional binary-cluster integral and vanishes at  $\Theta$ . In order to consider the effects of chain ends on  $A_3$ , it is necessary to introduce nine kinds of *excess* ternary-cluster integrals associated with those trios of beads which include at least one end bead. Note that there are ten kinds of ternary-cluster integrals in total, including the standard one ( $\beta_3$ ) for the trio only of intermediate beads. As explicitly shown later, the part  $A_3^{(E)}$  of  $A_3$  representing the effects of chain ends may be written in terms of three combinations  $\beta_{3,1}$ ,  $\beta_{3,2}$ , and  $\beta_{3,3}$  of the nine excess ternary-cluster integrals. The HW model itself is defined in terms of three basic model parameters: the constant differential-geometrical curvature  $\kappa_0$  and torsion  $\tau_0$  of its characteristic helix and the static stiffness parameter  $\lambda^{-1}$ .

According to the HW theory,<sup>1,25</sup>  $A_3$  in general may be written in the form

**Table I.** Values of  $M_w$  and  $A_{3,\Theta}$  for atactic oligo- and poly( $\alpha$ -methylstyrene)s in cyclohexane at 30.5 °C

Sample	$M_w$	$10^4 A_{3,\Theta}$ (cm <sup>6</sup> mol/g <sup>3</sup> )	Sample	$M_w$	$10^4 A_{3,\Theta}$ (cm <sup>6</sup> mol/g <sup>3</sup> )
OAMS4	$5.30 \times 10^2$ <sup>a</sup>	20	AMS2	$2.48 \times 10^4$	4.7
OAMS5	$6.48 \times 10^2$	17	AMS5	$5.22 \times 10^4$	4.5
OAMS8	$1.04 \times 10^3$	14	AMS6	$6.46 \times 10^4$	4.8
OAMS10	$1.27 \times 10^3$	9.9	AMS11	$1.15 \times 10^5$	4.9
OAMS13	$1.60 \times 10^3$	7.3	AMS15	$1.46 \times 10^5$	5.0
OAMS19	$2.27 \times 10^3$	8.9	AMS24	$2.38 \times 10^5$	5.2
OAMS25	$2.96 \times 10^3$	7.5	AMS40	$4.07 \times 10^5$	4.7
OAMS33	$3.95 \times 10^3$	6.3	AMS80	$8.50 \times 10^5$	4.8
OAMS38	$4.57 \times 10^3$	6.7	AMS200	$2.06 \times 10^6$	4.4
OAMS67	$7.97 \times 10^3$	4.7	AMS320	$3.22 \times 10^6$	5.0
AMS1	$1.30 \times 10^4$	4.2	AMS550	$5.46 \times 10^6$	5.6

<sup>a</sup>The values of  $M_w$  have been reproduced from refs 7 and 29.

**Table II.** Values of  $A_3$  and  $\alpha_S^3$  for atactic oligo- and poly( $\alpha$ -methylstyrene)s in toluene at 25.0 °C, in 4-*tert*-butyltoluene at 25.0 °C, and in *n*-butyl chloride at 25.0 °C

Sample	Toluene, 25.0 °C		4- <i>tert</i> -Butyltoluene, 25.0 °C		<i>n</i> -Butyl chloride, 25.0 °C	
	$10^2 A_3$ (cm <sup>6</sup> mol/g <sup>3</sup> )	$\alpha_S^3$	$10^2 A_3$ (cm <sup>6</sup> mol/g <sup>3</sup> )	$\alpha_S^3$	$10^2 A_3$ (cm <sup>6</sup> mol/g <sup>3</sup> )	$\alpha_S^3$
OAMS5	0.3 <sub>4</sub>	1 <sup>a</sup>				
OAMS8	0.3 <sub>7</sub>	1				
OAMS10	0.2 <sub>7</sub>	1				
OAMS13	0.2 <sub>7</sub>	1.00 <sup>b</sup>				
OAMS25	0.2 <sub>3</sub>	1.02				
OAMS33	0.2 <sub>0</sub>	1.03				
OAMS67	0.2 <sub>1</sub>	1.12				
AMS1	0.2 <sub>4</sub>	1.23				
AMS2	0.3 <sub>0</sub>	1.41				
AMS5	0.4 <sub>0</sub>	1.73				
AMS15	0.6 <sub>1</sub>	2.22				
AMS24	0.7 <sub>5</sub>	2.54	0.14	1.49	0.09	1.37
AMS40	1.0 <sub>7</sub>	3.11	0.18	1.63	0.13	1.55
AMS80	1.5 <sub>7</sub>	3.81	0.28	1.94	0.17	1.69
AMS200	2.5 <sub>6</sub>	4.69	0.45	2.30	0.30	2.02
AMS320	3.4 <sub>5</sub>	5.67	0.59	2.74	0.33	2.26
AMS550	4.7 <sub>2</sub>	6.60	0.78	3.19	0.44	2.48

<sup>a</sup>The values of  $\alpha_S^3$  for OAMS5, OAMS8, OAMS10 have been assumed to be 1 as in ref 7. <sup>b</sup>The values of  $\alpha_S^3$  for OAMS13 through AMS550 have been reproduced from refs 7 and 28.

$$A_3 = A_{3,\beta}^{(HW)} + \Delta A_3^{(HW)} + A_{3,\beta_3}^{(1)} \quad (1)$$

where  $A_{3,\beta}^{(HW)}$  is the part of  $A_3$  dependent only on  $\beta$ ,  $A_{3,\beta_3}^{(1)}$  is the part of  $A_3$  involving terms linear in the above-mentioned ternary-cluster integrals and independent of  $\beta$ , and  $\Delta A_3^{(HW)}$  is the remaining part of  $A_3$ . The terms  $A_{3,\beta}^{(HW)}$  and  $\Delta A_3^{(HW)}$  vanish at the  $\Theta$  temperature,<sup>26,30</sup> at which  $\beta$  vanishes, so that  $A_{3,\Theta}$  ( $A_3$  at  $\Theta$ ) is given by

$$A_{3,\Theta} = A_{3,\beta_3}^{(1)} \quad (2)$$

The term  $A_{3,\beta_3}^{(1)}$  may be written in the form

$$A_{3,\beta_3}^{(1)} = A_3^0 + A_3^{(E)} \quad (3)$$

The first term  $A_3^0$  is linear in  $\beta_3$  (free from the effects of chain ends) and is explicitly given by

$$A_3^0 = \frac{N_A^2 n^3 \beta_3}{3M^3} = \frac{N_A^2 c_\infty^3 L^3 B_3}{3M^3} \quad (4)$$

where  $N_A$  is the Avogadro constant,  $M$  is the molecular weight, and  $B_3$  is defined by

$$B_3 = \frac{\beta_3}{a^3 c_\infty^3} \quad (5)$$

with

$$c_\infty = \frac{4 + (\lambda^{-1} \tau_0)^2}{4 + (\lambda^{-1} \kappa_0)^2 + (\lambda^{-1} \tau_0)^2} \quad (6)$$

The second term  $A_3^{(E)}$  on the right-hand side of eq 3 is the sum of terms linear in the nine excess ternary-clus-

ter integrals and may be written in the form

$$A_3^{(E)} = a_{3,1} M^{-1} + a_{3,2} M^{-2} + a_{3,3} M^{-3} \quad (7)$$

where the coefficients  $a_{3,1}$ ,  $a_{3,2}$ , and  $a_{3,3}$  may be written in terms of the above-mentioned combinations  $\beta_{3,1}$ ,  $\beta_{3,2}$ , and  $\beta_{3,3}$  of the excess ternary-cluster integrals as follows

$$\begin{aligned} a_{3,1} &= 2N_A^2 \beta_{3,1} / M_0^2 \\ a_{3,2} &= 4N_A^2 \Delta \beta_{3,2} / M_0 \\ a_{3,3} &= (8/3)N_A^2 \Delta \beta_{3,3} \end{aligned} \quad (8)$$

with  $M_0$  the molecular weight of the bead and with

$$\begin{aligned} \Delta \beta_{3,2} &= \beta_{3,2} - 2\beta_{3,1} \\ \Delta \beta_{3,3} &= \beta_{3,3} - 3\beta_{3,2} + 3\beta_{3,1} \end{aligned} \quad (9)$$

We note that  $\beta_{3,1}$ ,  $\beta_{3,2}$ , and  $\beta_{3,3}$  are linear combinations of the excess ternary-cluster integrals associated with two kinds of trios of two intermediate beads and one end bead, with three kinds of trios of one intermediate bead and two end beads, and with four kinds of trios only of end beads, respectively.

For good-solvent systems, it is convenient to introduce a dimensionless factor  $g$  defined by<sup>31</sup>

$$g \equiv \frac{A_3}{[A_2^{(HW)}]^2 M} = g_2 + \Delta g_2 + g_3 \quad (10)$$

where  $A_2^{(HW)}$  is the part of  $A_2$  without the effects of chain ends,<sup>1</sup> and  $g_2$ ,  $\Delta g_2$ , and  $g_3$  are  $A_{3,\beta}^{(HW)}$ ,  $\Delta A_3^{(HW)}$ , and  $A_{3,\beta_3}^{(1)}$ , respectively, divided by  $[A_2^{(HW)}]^2 M$ . As

mentioned in the previous paper,<sup>9</sup> the (residual) contribution of three-segment interactions to  $A_2^{(HW)}$  may be ignored for good-solvent systems. Then  $A_2^{(HW)}$  and therefore  $g_2$  are functions only of  $\beta$  for those systems. It is known that  $\Delta g_2$  and  $g_3$  decrease with increasing  $M$ , and that the contribution  $\Delta g_2$  is smaller than that of  $g_3$ .<sup>1,30</sup> Thus, in what follows, we neglect  $\Delta g_2$ , for simplicity.

There must in general be some effects of chain stiffness on the quantity  $g_2$  in the second of eq 10, which is explicitly given by

$$g_2 = \frac{A_{3,\beta}^{(HW)}}{[A_2^{(HW)}]^2 M} \quad (11)$$

since its effects are remarkable on  $A_2^{(HW)}$ , as mentioned in the Introduction, and so more or less on  $A_3$ . For the reasons mentioned later, however, we simply adopt an approximate closed expression for  $g_2$  within the framework of the two-parameter (TP) theory without consideration of chain stiffness, *i.e.*,

$$g_2(\bar{z}) = 2.219\bar{z}(1 + 18\bar{z} + 12.6\bar{z}^2)^{-0.5} \quad (12)$$

with

$$\bar{z} = z/\alpha_S^3 \quad (13)$$

where  $z$  is the conventional excluded-volume parameter<sup>1,23</sup> defined in terms of  $\beta$  in place of  $\beta_2$ , and  $\alpha_S$  may be given by the Domb–Barrett equation<sup>32</sup>

$$\alpha_S^2 = [1 + 10z + (70\pi/9 + 10/3)z^2 + 8\pi^{3/2}z^3]^{2/15} \times [0.933 + 0.067 \exp(-0.85z - 1.39z^2)] \quad (14)$$

Equation 12 with eqs 13 and 14 has been empirically constructed by Norisuye *et al.*<sup>26</sup> so that it gives the correct TP theory relation<sup>23</sup>  $g_2 = 2.219\bar{z}$  in the limit of  $\bar{z} \rightarrow 0$  and also the asymptotic value  $5/8$  for rigid spheres in the limit of  $\bar{z} \rightarrow \infty$ , and further well reproduces the SC theory values<sup>22</sup> 0.108, 0.185, 0.28, and 0.36 of  $g_2$  at  $\bar{z} = 3^{3/2}/2$ ,  $3^{3/2}$ ,  $2 \times 3^{3/2}$ , and  $4 \times 3^{3/2}$ , respectively, as closely as possible.

From the second of eq 10 with eqs 3 and 4, the

term  $g_3$  may be written in the form

$$g_3 = \frac{4B_3}{3LB^2h^2} \left( 1 + \frac{A_3^{(E)}}{A_3^0} \right) \quad (15)$$

where we have used the HW theoretical expression<sup>1</sup> for  $A_2^{(HW)}$

$$A_2^{(HW)} = (N_A c_\infty^{3/2} L^2 B / 2M^2) h \quad (16)$$

with  $B$  the excluded-volume strength defined by

$$B = \frac{\beta}{a^2 c_\infty^{3/2}} \quad (17)$$

The so-called  $h$  function in eq 16 is given by

$$h(\hat{z}) = (1 + 7.74\hat{z} + 52.3\hat{z}^{27/10})^{-10/27} \quad (18)$$

with

$$\hat{z} = \tilde{z}/\alpha_S^3 \quad (19)$$

The intermolecular scaled excluded-volume parameter  $\tilde{z}$  is defined by

$$\tilde{z} = [Q(\lambda L)/2.865]z \quad (20)$$

where the coefficient  $Q(L)$  as a function of (reduced)  $L$  represents the effects of chain stiffness on  $A_2$ , as explicitly given below, and  $z$  is defined in terms of the HW model parameters by

$$z = (3/2\pi)^{3/2} (\lambda B)(\lambda L)^{1/2} \quad (21)$$

According to the quasi-two-parameter scheme or the Yamakawa–Stockmayer–Shimada theory,<sup>1,33–35</sup>  $\alpha_S$  in eq 19 may be given by the Domb–Barrett equation 14 with the intramolecular scaled excluded-volume parameter  $\tilde{z}$  defined by

$$\tilde{z} = \frac{3}{4} K(\lambda L)z \quad (22)$$

in place of  $z$ . In eq 22, the coefficient  $K(L)$  as a function of (reduced)  $L$  represents the effects of chain stiffness on the intramolecular excluded-volume effect and is given by

$$K(L) = \begin{cases} \frac{4}{3} - 2.711L^{-1/2} + \frac{7}{6}L^{-1} & \text{for } L > 6 \\ L^{-1/2} \exp(-6.611L^{-1} + 0.9198 + 0.03516L) & \text{for } L \leq 6 \end{cases} \quad (23)$$

The coefficient  $Q(L)$  in eq 20 is given for (reduced)  $L \gtrsim 1$  by<sup>1,8</sup>

$$Q(L) = -\frac{128\sqrt{2}}{15} - 2.531L^{-1/2} - 2.586L^{-1} + 1.985L^{-3/2} - 1.984L^{-2} - 0.9292L^{-5/2} + 0.1223L^{-3} + \frac{8}{5}x^{5/2} + \frac{2}{3}x^{3/2} \left( 8 + \frac{1}{6}L^{-1} \right) + x^{1/2}(8 - 13.53L^{-1} + 0.2804L^{-2}) - x^{-1/2}L^{-1}(0.3333 - 5.724L^{-1} + 0.7974L^{-2}) - x^{-3/2}L^{-2}(0.3398 - 0.7146L^{-1}) \quad (24)$$

with

$$x = 1 + 0.961L^{-1} \quad (25)$$

We simply put  $h = 1$  (rod limit) for  $\lambda L \lesssim 1$ , in which range eq 24 is not valid.

Finally, we consider the effects of chain stiffness on  $g_2$ . For the HW bead model, the quantities  $\alpha_S^2$ ,  $h$ , and  $A_{3,\beta}^{(HW)}$  may be expanded in terms of  $\beta$  as follows<sup>1</sup>

$$\alpha_S^2 = 1 + [67K(\lambda L)/70]z + \dots \quad (26)$$

$$h = 1 - Q(\lambda L)z + \dots \quad (27)$$

$$A_{3,\beta}^{(HW)} = \frac{N_A^2 c_\infty^3 L^4 B^2}{4M^3} U(\lambda L)z(1 + \dots) \quad (28)$$

where the (residual) effects of three-segment interactions have been ignored in  $\alpha_S^2$  and  $A_2^{(HW)}$  (or  $h$ ) since we here restrict ourselves to good-solvent systems, and the factor  $U(\lambda L)$  (strictly  $U/2.219$ ) on the right-hand side of eq 28 as a function of the reduced contour length  $\lambda L$  represents the effects of chain stiffness on the leading term of  $A_{3,\beta}^{(HW)}$ . Substitution of eqs 16 and 28 with eq 27 into eq 11 leads to

$$g_2 = U(\lambda L)z\{1 + [2Q(\lambda L) + \dots]z + \dots\} \quad (29)$$

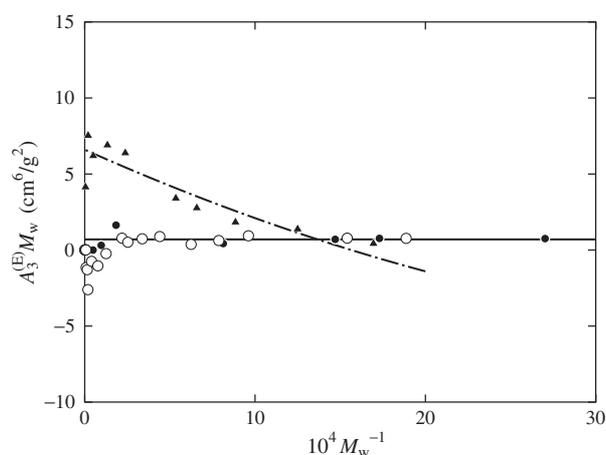
Norisuye *et al.*<sup>26</sup> have introduced the new scaled excluded-volume parameter  $\check{z}$  defined by

$$\check{z} = [U(\lambda L)/2.219]\bar{z} \quad (30)$$

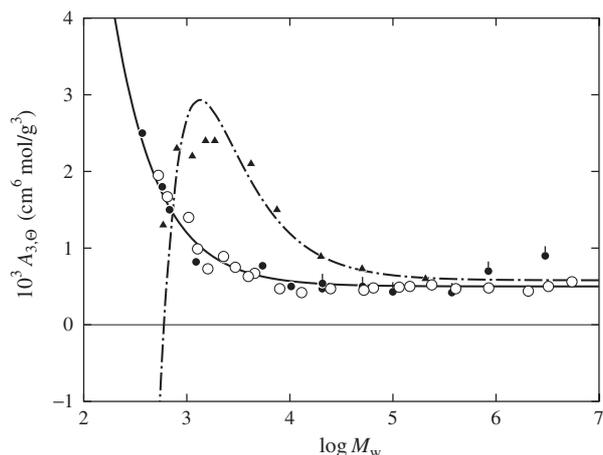
in order to take account of the effects of chain stiffness on  $g_2$  on the apparent analogy of the scaled parameters  $\check{z}$  and  $\check{\check{z}}$  defined by eqs 22 and 20, respectively. From a comparison of eqs 29 and 30 with eqs 20, 22, 26, and 27, it is seen that the scale factor in  $\check{z}$  arises from the zeroth-order term in the perturbation expansion, while those in  $\bar{z}$  and  $\check{\check{z}}$  arise from the first-order terms. Therefore, their expression for  $g_2$  given by eq 12 with  $\check{z}$  in place of  $\bar{z}$  provides an approximation, but it is not consistent with the maneuver of replacing  $z$  by  $\bar{z}$  and  $\check{\check{z}}$  in eqs 14 and 18 with  $\hat{z} = \bar{z}$ , respectively. [Recall that the first-order deviations of  $K(L)$  and  $Q(L)$  from their coil-limiting values are of order  $L^{-1/2}$ , as seen from eqs 23 and 24, while that of  $U(L)$  is of order  $L^{-1}$ .<sup>1,26</sup>] However, they have concluded that the effects of chain stiffness on  $g_2$  so considered are rather small. At any rate, this conclusion itself seems true, considering the fact that the effects of chain stiffness on  $A_2$  and  $A_3$  cancel, to some extent, each other in  $g_2$ . These are the reasons why we have simply adopted the (approximate) TP theoretical expression 12 for  $g_2$  without consideration of those effects. As shown later, eq 12 can indeed better explain experimental results than that with  $\check{z}$  in place of  $\bar{z}$ .

### Effects of Chain Ends

We begin by analyzing the data for  $A_{3,\Theta}$  for a-P $\alpha$ MS in cyclohexane at 30.5 °C given in Table I by the use of eq 2 with eqs 3, 4, and 7. The theory predicts that  $A_{3,\Theta}$  becomes a constant equal to  $A_3^0$  independent of  $M_w$  for such large  $M_w$  where  $A_3^{(E)}$  ( $\propto M_w^{-1}$  for large  $M_w$ ) becomes negligibly small. As mentioned above, the present data are consistent with this prediction, and  $A_3^0$  may be estimated to be  $5.0 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$  as a mean of values of  $A_{3,\Theta}$  for the six samples with the largest  $M_w$  given in Table I. The part  $A_3^{(E)}$  of  $A_3$  may then be calculated by subtracting this value of  $A_3^0$  from the observed values of  $A_{3,\Theta}$ . The values of  $A_3^{(E)}M_w$  so obtained for a-P $\alpha$ MS in cyclohexane at 30.5 °C are plotted against  $M_w^{-1}$  in Figure 1 (unfilled circles), where we have omitted the data points for the samples with  $M_w > 2 \times 10^5$  since the experimental error in  $A_3^{(E)}M_w$  increases with increasing  $M_w$ . For comparison, there are also shown the previous results for a-PS in cyclohexane at 34.5 °C<sup>25</sup> (filled circles) and a-PMMA in acetonitrile at 44.0 °C<sup>25</sup> (filled triangles). For a-PS and a-PMMA,<sup>25</sup> the respective values  $5.0 \times 10^{-4}$  and  $5.8 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$  of  $A_3^0$  have been used in the calculation of  $A_3^{(E)}$ . We note that for a-PS the value of  $A_3^0$  has been changed from  $4.7 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$  previously<sup>25</sup> adopted to the above one since the values of  $A_3$  for a-PS cannot be distinguished from those for a-P $\alpha$ MS beyond experimental error (see Figure 2). We also note that the values of  $\beta_3$  per repeat unit are estimated to be  $6.8 \times 10^{-45}$ ,  $4.7 \times 10^{-45}$ , and  $4.8 \times 10^{-45} \text{ cm}^6$  for a-P $\alpha$ MS, a-PS, and a-PMMA, respectively, from eq 4 with the above-given values of  $A_3^0$ , where the repeat unit has



**Figure 1.** Plots of  $A_3^{(E)}M_w$  against  $M_w^{-1}$ : (○) present data for a-P $\alpha$ MS in cyclohexane at 30.5 °C (●) a-PS in cyclohexane at 34.5 °C;<sup>25</sup> (▲) a-PMMA in acetonitrile at 44.0 °C (○).<sup>25</sup> The solid horizontal straight line fits the data points for both a-P $\alpha$ MS and a-PS, and the dot-dashed curve represents the theoretical values for a-PMMA calculated from eq 7 (see the text).

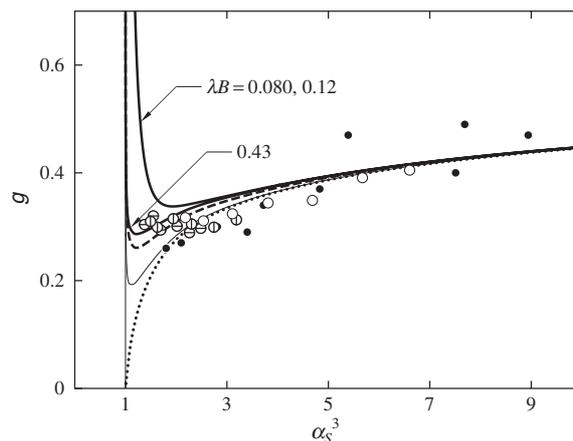


**Figure 2.** Plots of  $A_{3,\Theta}$  against  $\log M_w$  for a-P $\alpha$ MS in cyclohexane at 30.5 °C, a-PS in cyclohexane at 34.5 °C,<sup>25</sup> and a-PMMA in acetonitrile at 44.0 °C,<sup>25</sup> including literature data (●) for a-PS in cyclohexane at 34.5 °C by Nakamura *et al.*<sup>13</sup> The other symbols have the same meaning as those in Figure 1. The solid curve represents the theoretical values for both a-P $\alpha$ MS and a-PS calculated from eq 2 with eqs 3 and 7, and the dot-dashed curve, those for a-PMMA (see the text).

been taken as a single bead, *i.e.*,  $M_0(=M/n) = 118, 104,$  and  $100$  for a-P $\alpha$ MS, a-PS, and a-PMMA, respectively.

It is seen from Figure 1 that the data points for both a-P $\alpha$ MS and a-PS follow the common horizontal straight line (solid line), so that we may put  $a_{3,2} = a_{3,3} = 0$  in eq 7 and assign the value  $0.70 \text{ cm}^6/\text{g}^2$  to  $a_{3,1}$  for them. In contrast to the cases of a-P $\alpha$ MS and a-PS, the data points for a-PMMA follow a curve slightly concave upward. The dot-dashed curve represents the best-fit theoretical values for a-PMMA calculated from eq 7 with the respective values  $6.6 \text{ cm}^6/\text{g}^2$ ,  $-5 \times 10^3 \text{ cm}^6/\text{g mol}$ , and  $5 \times 10^5 \text{ cm}^6/\text{mol}^2$  of  $a_{3,1}$ ,  $a_{3,2}$ , and  $a_{3,3}$  previously<sup>25</sup> assigned. We may then calculate  $\beta_{3,1}$ ,  $\beta_{3,2}$ , and  $\beta_{3,3}$  from eqs 8 and 9 with the above-determined values of  $a_{3,1}$ ,  $a_{3,2}$ , and  $a_{3,3}$ . The respective values of  $\beta_{3,1}$ ,  $\beta_{3,2}$ , and  $\beta_{3,3}$  so calculated are  $1.3 \times 10^{-44}$ ,  $2.7 \times 10^{-44}$ , and  $4.0 \times 10^{-44} \text{ cm}^6$  for a-P $\alpha$ MS,  $1.0 \times 10^{-44}$ ,  $2.1 \times 10^{-44}$ , and  $3.1 \times 10^{-44} \text{ cm}^6$  for a-PS, and  $9.1 \times 10^{-44}$ ,  $-1.6 \times 10^{-43}$ , and  $-2.4 \times 10^{-43} \text{ cm}^6$  for a-PMMA, where the repeat unit has been taken as a single bead as above.

For a comparison of theory with experiment, in Figure 2 are shown plots of  $A_{3,\Theta}$  against  $\log M_w$ . As in Figure 1, the unfilled circles represent the present experimental values for a-P $\alpha$ MS in cyclohexane at 30.5 °C, and the filled circles and triangles, the previous ones for a-PS in cyclohexane at 34.5 °C<sup>25</sup> and a-PMMA in acetonitrile at 44.0 °C,<sup>25</sup> respectively, where the filled circles with pip represent the values obtained by Nakamura *et al.*<sup>13</sup> The solid curve represents the theoretical values for both a-P $\alpha$ MS and a-PS,



**Figure 3.** Plots of  $g$  against  $\alpha_S^3$ : (○) present data for a-P $\alpha$ MS in toluene at 25.0 °C; (⊙) present data for a-P $\alpha$ MS in 4-*tert*-butyltoluene at 25.0 °C; (⊕) present data for a-P $\alpha$ MS in *n*-butyl chloride at 25.0 °C; (●) literature data for a-PS in benzene at 25.0 °C by Sato *et al.*<sup>11</sup> and by Nakamura *et al.*<sup>12</sup> The heavy solid curves represent the theoretical values of  $g = g_2 + g_3$  for a-P $\alpha$ MS for the indicated values of  $\lambda B$ , and the dashed curve, those for a-PS. The light solid curve represents the theoretical values of  $g = g_2 + g_3$  with  $h = 1$  for a-P $\alpha$ MS for  $\lambda B = 0.43$ . The dotted curve represents the TP (or SC) theory values of  $g_2$  (see the text).

and the dot-dashed curve, those for a-PMMA, which have been calculated from eq 2 with eqs 3 and 7 with the above-given values of  $A_3^0$  and  $a_{3,i}$  ( $i = 1, 2, 3$ ). Agreement between theory and experiment is satisfactory, indicating that the dependence of  $A_{3,\Theta}$  on  $M_w$  arises definitely from the effects of chain ends.

For convenience, we here make a brief mention of the dependence on temperature of  $\beta_3$  of a-P $\alpha$ MS near the  $\Theta$  temperature, showing explicitly no experimental data. Nakamura *et al.*<sup>16</sup> have estimated values of  $\beta_3$  for a-PS in *trans*-decalin near the  $\Theta$  temperature (21 °C) and shown that  $\beta_3$  is independent of temperature there. We have made an analysis of data for  $A_3$  in cyclohexane at temperatures ranging from 15.0 to 45.0 °C in a similar manner but with the values of  $\beta$  previously<sup>29</sup> determined (not proportional to  $1 - \Theta/T$  with  $T$  the absolute temperature), and found that  $\beta_3$  of a-P $\alpha$ MS in cyclohexane in this range is also independent of temperature, as previously<sup>29</sup> assumed.

#### Effects of Three-segment Interactions

Now we examine the behavior of the factor  $g$  of a-P $\alpha$ MS in the three good solvents, toluene, 4-*tert*-butyltoluene, and *n*-butyl chloride, and make a comparison of experimental values with theoretical ones from eq 10 with  $\Delta g_2 = 0$  and with eqs 12–15 and 18–25. Although there must exist effects of chain ends on  $A_3$  as well as on  $A_2$  also in the good solvents as in the  $\Theta$  solvent, it is difficult to estimate the contribution  $A_3^{(E)}$  of the effects separately from the others. The situation is different from that in  $A_2$ . We therefore

restrict ourselves to the range of  $M_w \gtrsim 10^5$  in which the effects on  $A_2$  and  $A_3$  may be ignored, so that  $A_2 = A_2^{(\text{HW})}$  and  $A_3^{(\text{E})} = 0$ .

Figure 3 shows plots of  $g$  against  $\alpha_S^3$  for the a-P $\alpha$ MS samples with  $M_w > 10^5$  in toluene (unfilled circles), 4-*tert*-butyltoluene (unfilled circles with vertical line segment), and *n*-butyl chloride (unfilled circles with horizontal line segment) at 25.0 °C. Here, the  $g$  values have been calculated from the first of eq 10 with the values of  $M_w$  and  $A_3$  given in Table I and II, respectively, and with those of  $A_2$  given in Table II of ref 7. For comparison, literature data (filled circles) by Sato *et al.*<sup>11</sup> and by Nakamura *et al.*<sup>12</sup> for a-PS samples with  $M_w \gtrsim 10^5$  in benzene at 25.0 °C are also plotted. It is seen that all the data points form nearly a single-composite curve within experimental error.

In the figure, the dotted curve represents the values of  $g_2$  calculated from eq 12 with eqs 13 and 14, which correspond to the TP (or SC) theory values without consideration of chain stiffness, as mentioned above. The heavy solid curves represent the values of  $g = g_2 + g_3$  for a-P $\alpha$ MS for the indicated values of  $\lambda B$ , and the dashed curve, those for a-PS, which have been obtained by adding the above-calculated values of  $g_2$  to those of  $g_3$  from eq 15 with  $A_3^{(\text{E})} = 0$  and with eqs 14 and 18–25 with  $\tilde{z}$  in place of  $z$  in eq 14. We note that the values 0.43, 0.12, and 0.080 of  $\lambda B$  have been determined from  $\alpha_S^2$  for a-P $\alpha$ MS in toluene, 4-*tert*-butyltoluene, and *n*-butyl chloride, respectively, at 25.0 °C, and that the curves for a-P $\alpha$ MS for  $\lambda B = 0.12$  and 0.080 are not clearly separated from each other. The light solid curve represents the values of  $g = g_2 + g_3$  for a-P $\alpha$ MS in toluene obtained with the values of  $g_3$  from eq 15 with  $A_3^{(\text{E})} = 0$  and  $h = 1$  (the single-contact approximation to  $A_2$ ). The values of the HW model parameters used for the calculation of  $g_3$  for a-P $\alpha$ MS are  $\lambda^{-1}\kappa_0 = 3.0$ ,  $\lambda^{-1}\tau_0 = 0.9$ , and  $\lambda^{-1} = 46.8 \text{ \AA}$ , which have been determined from the unperturbed mean-square radius of gyration  $\langle S^2 \rangle_0$ ,<sup>27</sup> along with the above-given values of  $\lambda B$  and  $\lambda^3 B_3 = 0.060$ . We note that  $\lambda^3 B_3$  has been calculated from eq 4 with the above-given value  $5.0 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$  of  $A_3^0$  and the value<sup>27</sup>  $39.8 \text{ \AA}^{-1}$  of the shift factor<sup>1,2</sup>  $M_L (=M/L)$  as defined as the molecular weight per unit contour length, assuming that the solvent dependence of  $\beta_3$  is small. [However, note that the (residual) contribution of  $\beta_3$  itself (and hence  $g_3$ ) cannot be ignored even for good-solvent systems, although probably smaller than that in the  $\Theta$  solvent,<sup>9</sup> in contrast to the case of  $A_2$  (see Figure 3 and also below).] The values of the HW model parameters used for a-PS are  $\lambda^{-1}\kappa_0 = 3.0$ ,  $\lambda^{-1}\tau_0 = 6.0$ , and  $\lambda^{-1} = 20.6 \text{ \AA}$ , which have been determined from  $\langle S^2 \rangle_0$ ,<sup>1,36</sup> along with  $\lambda B = 0.33$  and  $\lambda^3 B_3 = 0.040$ , the value of  $\lambda^3 B_3$  hav-

ing been calculated from eq 4 with  $A_3^0 = 5.0 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$  and  $M_L = 35.8 \text{ \AA}^{-1}$ .<sup>1,36</sup>

The theoretical curves for a-P $\alpha$ MS for the different values of  $\lambda B$  (heavy solid curves) and for a-PS (dashed curve) are clearly separated from each other as  $\alpha_S^3$  is decreased from *ca.* 3 to 1. In the range of  $\alpha_S^3$  in which the data points are plotted ( $M_w \gtrsim 10^5$ ), however, the separation of the curves is rather small, and they form nearly a single-composite curve, being consistent with the above-mentioned behavior of the experimental data. It is seen that the upward deviation of the data points from the dotted curve ( $g_2$ ) for  $\alpha_S^3 \lesssim 2$  is mainly due to the contribution of  $g_3$ , *i.e.*, the effects of three-segment interactions, indicating that the effects of chain stiffness on  $g_2$  are of minor importance. If the latter effects are considered, as done by Norisuye *et al.*,<sup>26</sup> then the theoretical values of  $g$  are appreciably overestimated for  $\alpha_S^3 \lesssim 2$ . Further, the single-contact approximation  $h = 1$  to  $A_2$  (light solid curve) made by them in the calculation of  $g_3$  is not justified, as seen from the difference between the heavy solid curve for  $\lambda B = 0.43$  and the light solid curve for  $\alpha_S^3 \lesssim 2$ . However, we note that our theoretical values of  $g_3$  and therefore still  $g$  are slightly overestimated for  $\alpha_S^3 \lesssim 2$  because of the possible overestimate of the values of  $\beta_3$  assumed for good-solvent systems<sup>9</sup> or of the fact that eq 18 somewhat underestimates  $h$  (or  $\Psi$ ) (see Figures 8 and 9 of ref 7).

## CONCLUSIONS

We have analyzed  $A_3$  data obtained from the previous LS measurements for a-P $\alpha$ MS over a wide range of  $M_w$ , including the oligomers with very small  $M_w$ , in both  $\Theta$  and good solvents on the basis of the HW chain model. It has been found that  $A_{3,\Theta}$  in cyclohexane at 30.5 °C becomes a constant of  $5.0 \times 10^{-4} \text{ cm}^6 \text{ mol/g}^3$  independent of  $M_w$  for  $M_w \gtrsim 10^4$  and deviates from it for  $M_w \lesssim 10^4$  as in the cases of a-PS and a-PMMA previously<sup>25</sup> studied. The observed dependence of  $A_{3,\Theta}$  on  $M_w$  may be well explained by the HW theory that takes account of the effects of chain ends. For good-solvent systems, the behavior of the factor  $g \equiv A_3/[A_2^{(\text{HW})}]^2 M_w$  as a function of  $\alpha_S^3$  in toluene, 4-*tert*-butyltoluene, and *n*-butyl chloride at 25.0 °C has been examined. It has then been found that the present data points for the a-P $\alpha$ MS samples with  $M_w \gtrsim 10^5$  together with those obtained by Sato *et al.*<sup>11</sup> and by Nakamura *et al.*<sup>12</sup> for a-PS in benzene at 25.0 °C form nearly a single-composite curve, being consistent with the HW theory prediction. As found by Norisuye *et al.*,<sup>26</sup> the observed values of  $g$  (for  $M_w \gtrsim 10^5$ ) may be well explained by the TP (or SC) theory<sup>22</sup> for  $\alpha_S^3 \gtrsim 2$  but are appreciably larger than the latter values for  $\alpha_S^3 \lesssim 2$ . However, this disa-

greement arises mainly from the effects of three-segment interactions, the effects of chain stiffness being of minor importance.

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