

## ORIGINAL ARTICLE

# Intermolecular interactions of brush-like polymers

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The excluded-volume parameter  $B$  for brush-like polymers was calculated assuming that each brush-like segment consists of a straight main chain with Gaussian side chains. Interactions between brush-like segments were represented by the binary and ternary interactions among side-chain segments. The first-order perturbation calculation in terms of the binary interaction between side-chain segments gave a much larger value for  $B$  than the values determined from analyses of the second virial coefficient  $A_2$  of polystyrene polymacromonomers in toluene. This suggests that consideration of higher-order terms is necessary. Results based on the smoothed-density (SD) model gave much closer values to the experimental values. Perturbation calculations considering the ternary interactions among side-chain segments revealed that it is necessary to include the residual ternary interactions for theta solvent systems. This result contradicts the experimental observation that  $A_2$  for polystyrene polymacromonomers in cyclohexane vanishes at 34.5 °C. However, the calculated results based on the SD model showed that the contribution from the effects of the residual ternary interactions is within the experimental error.

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## INTRODUCTION

Comb-branched polymers with dense side chains are called brush-like polymers.<sup>1–3</sup> After the establishment of synthetic methods, the number of studies on such polymers increased because of their interesting properties, such as liquid crystallinity.<sup>4–6</sup> A typical method to obtain brush-like polymers is polymerization of macromonomers,<sup>7,8</sup> which consist of linear polymers with a polymerizable group at one end of the chain. From studies of polymacromonomers in solution, it was shown that these molecules behave as stiff chains.<sup>1,2,9–14</sup>

We have studied the dimensional properties of polymacromonomers consisting of polystyrene (PS) in a good solvent (toluene at 15.0 °C) and in a theta solvent (cyclohexane at 34.5 °C) and determined the stiffness parameter  $\lambda^{-1}$  as functions of the degree of polymerization of side chain,  $n_s$ .<sup>11–13,15–18</sup> The  $\lambda^{-1}$  values obtained for these polymers were explained by the first-order perturbation calculation in terms of segmental interactions among side chains.<sup>19</sup> It was also shown that the polymacromonomer chains expand because of intramolecular excluded-volume effects in a good solvent,<sup>12,13</sup> when the main chain is sufficiently long compared with the Kuhn segment length or  $\lambda^{-1}$ . The magnitude of these effects are quantified by the excluded-volume parameter  $B$ ,<sup>20,21</sup> which represents the excluded volume of a pair of segments divided by the square of the segment length. The  $B$  values were obtained from the radius expansion factor and found to increase with the side-chain length. The interaction between polymacromonomer segments may be described as a sum of segmental interactions among side chains.

In the calculation of  $\lambda^{-1}$  for brush-like polymers, the polymer molecule was modeled by a wormlike main chain with Gaussian side

chains.<sup>19</sup> Essentially the same model, a straight main chain with Gaussian side chains, may be used for the brush-like segment, which is an interacting unit of brush-like polymers. Interactions between two brush-like segments may be described by a sum of the interactions among side-chain beads. Because two side chains that belong to different brush-like segments contact at a place apart from the main chains, interactions between these segments are long-ranged. Thus, the problem is similar to segment–segment interactions of polyelectrolytes.<sup>22</sup>

The second virial coefficient  $A_2$  is also a reflection of the interaction between segments. Here, previously obtained data of  $A_2$  for PS polymacromonomers in toluene<sup>11,15,18</sup> are analyzed to determine  $B$  values for different side-chain lengths. The values obtained for  $B$  are compared with the theoretical results calculated by the perturbation and the smoothed-density (SD) methods.

## THEORIES

### Basic equations

The brush-like segment is modeled by a straight main chain of length  $a$  with Gaussian side chains connected to it at intervals of  $h_s$ . Each side chain consists of  $n_s$  beads connected by bonds of length  $b$ .

The excluded volume for a pair of brush-like segments may be given by<sup>22</sup>

$$v = \int \langle 1 - e^{-W_{12}(\mathbf{r})/k_B T} \rangle d\mathbf{r} \quad (1)$$

The inter-segment potential  $W_{12}(\mathbf{r})$  depends on the directions of the main chains of the segments as well as the distance  $\mathbf{r}$  between the middle points of the main chains. The angular brackets of the

above equation signify averaging over the relative direction of these segments. The excluded-volume parameter  $B$  is defined by

$$B = \nu/a^2 \quad (2)$$

The distance and directions of two brush-like segments are illustrated in Figure 1. The first brush-like segment (segment 1) is assumed to lie along the  $z$  axis of the Cartesian coordinates with its center of mass at the origin  $O$ . The side chains are numbered from 1 to  $a/2h_s$  from the one closest to the origin for positive  $z$  and from  $-1$  to  $-a/2h_s$  for negative  $z$ . The side-chain beads (or segments) are numbered from 1 to  $n_s$  from the closest one to the main chain. Here, the number of side chains in one segment  $a/h_s$  and  $n_s$  are considered to be much larger than 1. The position of the center of the main chain of the second brush-like segment (segment 2) is represented by  $\mathbf{r}$ . The direction of segment 2 may be represented based on another set of Cartesian coordinates ( $x', y', z'$ ) with its origin fixed at the center of segment 2 and with each axis being parallel to the first set of Cartesian coordinates. The azimuthal and rotational angles around the  $z'$  axis are represented by  $\theta$  and  $\phi$ , respectively. The numbering of the side chains and the side-chain beads of segment 2 is same as that of segment 1.

The probability that the  $p_i$ th bead of the  $i$ th side chain of segment 1 lies between  $\mathbf{R}$  and  $\mathbf{R}+d\mathbf{R}$  may be given by the following Gaussian function:

$$P(\mathbf{R}; \mathbf{r}_i, p_i) d\mathbf{R} = \left( \frac{3}{2\pi b^2} \right)^{3/2} \exp \left[ -\frac{3(\mathbf{R} - \mathbf{r}_i)^2}{2p_i b^2} \right] d\mathbf{R} \quad (3)$$

Here,  $\mathbf{r}_i$  represents the position of the connecting point of the  $i$ th side chain to the main chain. A similar expression for  $P(\mathbf{R}; \mathbf{r}_j, q_j)$  for the  $q_j$ th bead of the  $j$ th side chain of segment 2 can be obtained, where  $\mathbf{r}_j$  represents the distance from the origin  $O$  to the connecting point of the  $j$ th side chain to the main chain of segment 2.

The probability density that two segments  $p_i$  and  $q_j$  are in contact can be calculated as<sup>19</sup>

$$\begin{aligned} P(\mathbf{0}_{p_i, q_j}; \mathbf{r}_{ij}, p_i, q_j) &= \int P(\mathbf{R}; \mathbf{r}_i, p_i) P(\mathbf{R}; \mathbf{r}_j, q_j) d\mathbf{R} \\ &= \left( \frac{3}{2\pi b^2} \right)^{3/2} \frac{1}{(p_i + q_j)^{3/2}} \exp \left[ -\frac{3r_{ij}^2}{2b^2(p_i + q_j)} \right] \end{aligned} \quad (4)$$

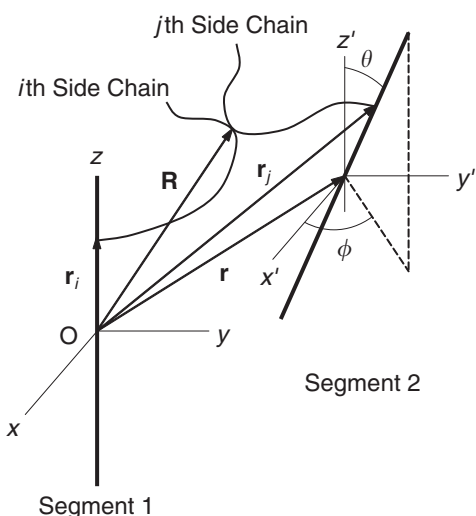


Figure 1 Coordinates of two brush-like segments.

Here,  $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$  and  $\mathbf{0}_{p_i, q_j}$  means that the distance between the segments  $p_i$  and  $q_j$  is zero. The vectors  $\mathbf{r}_i$  and  $\mathbf{r}_j - \mathbf{r}$  can be written as follows:

$$\mathbf{r}_i = (0, 0, ih_s)$$

$$\mathbf{r}_j - \mathbf{r} = (jh_s \sin \theta \cos \phi, jh_s \sin \theta \sin \phi, jh_s \cos \theta)$$

Thus,  $\mathbf{r}_{ij}$  is a function of  $\mathbf{r}$ ,  $i$ ,  $j$ ,  $\theta$ , and  $\phi$ , although it is not explicitly written.

### Binary-cluster approximation

*Perturbation calculation.* The potential for two brush-like segments  $W_{12}(\mathbf{r})$  may be expressed by the sum of the pair potentials  $w(\mathbf{u}_{p_i, q_j})$  between segments  $p_i$  and  $q_j$ , separated by  $\mathbf{u}_{p_i, q_j}$ .

$$W_{12}(\mathbf{r}) = \sum_{i,j} \sum_{p_i, q_j} w(\mathbf{u}_{p_i, q_j}) \quad (5)$$

Introducing the following function,

$$\chi_{p_i, q_j} = e^{-w(\mathbf{u}_{p_i, q_j})/k_B T} - 1 \quad (6)$$

equation (1) can be expanded as<sup>23</sup>

$$\nu = \sum_{i,j} \sum_{p_i, q_j} \int \langle \chi_{p_i, q_j} \rangle d\mathbf{r} + \sum_{i,j,k} \sum_{p_i, q_j, s_k} \int \langle \chi_{p_i, q_j} \chi_{p_i, s_k} \rangle d\mathbf{r} + \dots \quad (7)$$

Assuming short range interactions between segments,  $\chi_{p_i, q_j}$  may be replaced by  $-\beta_2 \delta(\mathbf{u}_{p_i, q_j})$  with the delta function, where  $\beta_2$  is the binary-cluster integral between side-chain beads. Then, the first term of the right-hand side of equation (7), designated by  $\nu_{2-1}$ , can be written as

$$\nu_{2-1} = \beta_2 \sum_{i,j} \sum_{p_i, q_j} \left\langle \int P(\mathbf{0}_{p_i, q_j}; \mathbf{r}_{ij}, p_i, q_j) d\mathbf{r} \right\rangle \quad (8)$$

Substituting equation (4) into the above equation,  $\nu_{2-1}$  is obtained as

$$\nu_{2-1} = \left( \frac{n_s a}{h_s} \right)^2 \beta_2 \quad (9)$$

This is an obvious result because  $(n_s a/h_s)^2$  represents the total number of cases that one bead of segment 1 and another bead of segment 2 are in contact as shown in 2-1 of Figure 2.

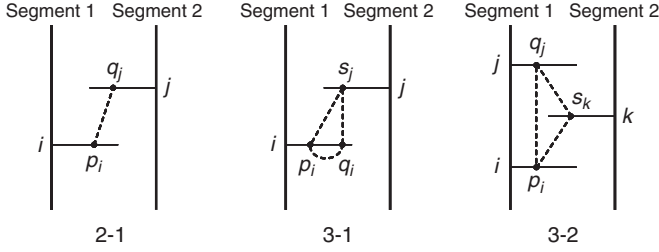
The second term of the right-hand side of equation (7) was also calculated. However, it was found that the absolute value of the second term is more than 10 times larger than the first term, indicating that the convergence of the power series is not good.

*Smoothed-density model.* Because the convergence of the perturbation calculation was not satisfactory,  $\nu$  is calculated according to the SD model. In this model, the inter-segment potential is written as<sup>23</sup>

$$\frac{W_{12}(\mathbf{r})}{k_B T} = \beta_2 \sum_{i,j} \sum_{p_i, q_j} P(\mathbf{0}_{p_i, q_j}; \mathbf{r}_{ij}, p_i, q_j) \quad (10)$$

Substituting the above equation with equation (4) into equation (1), the excluded-volume  $\nu_2^{\text{SD}}$  for this model is given by

$$\nu_2^{\text{SD}} = \int \left\langle 1 - \exp \left\{ -\beta_2 \sum_{i,j} \sum_{p_i, q_j} \left( \frac{3}{2\pi b^2} \right)^{3/2} \frac{1}{(p_i + q_j)^{3/2}} \exp \left[ -\frac{3r_{ij}^2}{2b^2(p_i + q_j)} \right] \right\} \right\rangle d\mathbf{r} \quad (11)$$



**Figure 2** Diagrammatic representation of interactions among side chains. Thick and thin solid lines indicate the main and side chains, respectively. Dashed lines connect interacting segments.

The sums over  $i$  and  $j$  may be approximated by integrals from  $-\infty$  to  $\infty$ . Further, the following assumption is made according to Fixman and Skolnick.<sup>22</sup> In Figure 1, the plane that is parallel to the  $z$  axis and contains the main chain of segment 2 is denoted as  $S$ . Assuming that the interaction between two brush-like segments occurs only when the projection of the main chain of segment 2 onto the  $xy$  plane crosses the perpendicular from the origin  $O$  to the plane  $S$ , the following is obtained:

$$v_2^{\text{SD}} = a^2 \int_0^\infty du \int_0^\pi d\theta \sin^2 \theta \left\{ 1 - \exp \left[ -\beta_2 \left( \frac{3}{2\pi b^2} \right)^{1/2} \frac{1}{h_s^2 \sin \theta} \sum_{p_i, q_j} \frac{1}{(p_i + q_j)^{1/2}} \right. \right. \\ \left. \left. \times \exp \left( -\frac{3}{2b^2(p_i + q_j)} u^2 \right) \right] \right\} \quad (12)$$

Here,  $u$  represents the distance between the origin and the plane  $S$ . After summing over  $p_i$  and  $q_j$ , the excluded-volume  $v_2^{\text{SD}}$  is obtained by numerical integration over  $u$  and  $\theta$ .

### Effects of ternary clustering

*Perturbation calculation.* It is known that ternary-cluster terms are not negligibly small at and near the theta point as the binary-cluster integral reduces to the same order of magnitude as the ternary-cluster integral.<sup>24</sup>

Here, two ternary-clustering terms are considered. The first is for the case that two beads of a side chain belonging to segment 1 and one bead belonging to segment 2 contact, as shown in 3-1 of Figure 2, where the side chain belonging to segment 1 makes a loop. The term for this case may be written as

$$v_{3-1} = 2\beta_3 \sum_{i,j} \sum_{p_i, q_i, s_j} \left\langle \int P(\mathbf{0}_{p_i, q_i}, \mathbf{0}_{p_i, s_j}; \mathbf{r}_{ij}, p_i, q_i, s_j) d\mathbf{r} \right\rangle \quad (13)$$

Here, the side chains  $i$  and  $j$  belong to segments 1 and 2, respectively. The segments  $p_i$  and  $q_j$  are on the side chain  $i$  and the segment  $s_j$  is on the side chain  $j$ . The factor of 2 comes from the two cases that the side chain making a loop belongs to segment 1 or 2. The probability density in equation (13) is obtained with the aid of the Wang-Uhlenbeck theory<sup>23,25</sup> as

$$P(\mathbf{0}_{p_i, q_i}, \mathbf{0}_{p_i, s_j}; \mathbf{r}_{ij}, p_i, q_i, s_j) = \left( \frac{3}{2\pi b^2} \right)^3 \frac{1}{(q_i - p_i)^{3/2} (p_i + s_j)^{3/2}} \\ \times \exp \left[ -\frac{3r_{ij}^2}{2b^2(p_i + q_i)} \right] \quad (14)$$

The sums in equation (13) over  $p_i$ ,  $q_i$  and  $s_j$  may be replaced by integrals from 0 to  $n_s$  and those over  $i$  and  $j$  may be replaced

by integrals from  $-\infty$  to  $\infty$ . After performing these integrations, along with those on  $\mathbf{r}$ ,  $\theta$  and  $\phi$ ,  $v_{3-1}$  is obtained as

$$v_{3-1} = \frac{4a^2 n_s^2}{h_s^2} \left( \frac{3}{2\pi b^2} \right)^{3/2} \left( \frac{1}{\sigma^{1/2}} - \frac{2}{n_s^{1/2}} \right) \beta_3 \quad (15)$$

Here,  $\sigma$  means the minimum number of segments for making a loop. If  $v_{3-1}$  is combined with  $v_{2-1}$ , the following is obtained:

$$v_{2-1} + v_{3-1} = \left( \frac{n_s a}{h_s} \right)^2 \left[ \beta_2 + 4 \left( \frac{3}{2\pi b^2} \right)^{3/2} \left( \frac{1}{\sigma^{1/2}} - \frac{2}{n_s^{1/2}} \right) \beta_3 \right] \quad (16)$$

The expression in the brackets of the above equation is the same as the one that appears in the second virial coefficient of linear polymers.<sup>24,26</sup> It is known that the negative  $\beta_2$  and the positive  $\beta_3$  terms cancel out at the theta point, where  $A_2$  becomes zero, by<sup>24,26</sup>

$$\beta_2 + \frac{4}{\sigma^{1/2}} \left( \frac{3}{2\pi b^2} \right)^{3/2} \beta_3 = 0$$

Thus, it is expected that the contribution from  $v_{2-1} + v_{3-1}$  to  $B$  vanishes at this point for sufficiently large  $n_s$ .

Next, the following case is considered: two beads belonging to different side chains of segment 1 and one bead belonging to segment 2 contact, as shown in 3-2 of Figure 2. The term for this case may be written as

$$v_{3-2} = 2\beta_3 \sum_{i,j,k} \sum_{p_i, q_j, s_k} \left\langle \int P(\mathbf{0}_{p_i, s_k}, \mathbf{0}_{q_j, s_k}; \mathbf{r}_{ik}, \mathbf{r}_{ij}, p_i, q_j, s_k) d\mathbf{r} \right\rangle \quad (17)$$

Here, the side chains  $i$  and  $j$  belong to segment 1 and the side chain  $k$  to segment 2. The factor of 2 appears for the same reason as in equation (13). The probability density for this case can be written as

$$P(\mathbf{0}_{p_i, q_j}, \mathbf{0}_{p_i, s_k}; \mathbf{r}_{ik}, \mathbf{r}_{ij}, p_i, q_j, s_k) = \left( \frac{3}{2\pi b^2} \right)^3 \frac{1}{(p_i q_j + q_j s_k + p_i s_k)^{3/2}} \\ \times \exp \left\{ -\frac{3}{2b^2(p_i q_j + q_j s_k + p_i s_k)} [q_j r_{ik}^2 + p_i r_{ij}^2 + s_k h_s^2 (j - i)^2] \right\} \quad (18)$$

Substituting equation (18) into equation (17),  $v_{3-2}$  is obtained as

$$v_{3-2} = (4 \ln 2) \frac{n_s^2 a^2}{h_s^3} \beta_3 \quad (19)$$

Here, all the summations were approximated by integrals.

*Smoothed-density model.* The contribution of the ternary-clustering to  $v$  may also be calculated by the SD model. If the interactions of three beads belonging to different side chains are considered, the potential for segments 1 and 2 may be given by

$$\frac{W_{12}(\mathbf{r})}{k_B T} = \beta_3 \sum_{i,j,k} \sum_{p_i, q_j, s_k} P(\mathbf{0}_{p_i, q_j}, \mathbf{0}_{p_i, s_k}; \mathbf{r}_{ik}, \mathbf{r}_{ij}, p_i, q_j, s_k) \quad (20)$$

From a similar argument to that of the SD model in the binary-cluster approximation, the following expression of  $v_3$  for this model is obtained:

$$v_3^{\text{SD}} = a^2 \int_0^\infty du \int_0^\pi d\theta \sin^2 \theta \left\{ 1 - \exp \left[ -2\beta_3 \left( \frac{3}{2\pi b^2} \right)^{3/2} \frac{1}{h_s^3 \sin \theta} \sum_{p_i, q_j, s_k} \frac{1}{[(p_i q_j + q_j s_k + p_i s_k)(p_i + q_j)]^{1/2}} \exp \left( -\frac{3(p_i + q_j)}{2b^2(p_i q_j + q_j s_k + p_i s_k)} u^2 \right) \right] \right\} \quad (21)$$

The factor of 2 in front of  $\beta_3$  in the above equation appears for the same reason as it does in equation (17).

## COMPARISON WITH EXPERIMENTS

### Good solvent systems

Previous  $A_2$  data for PS polymacromonomers with different side-chain lengths in toluene at 15.0 °C<sup>12,15,18</sup> are plotted against the weight-average molecular weight  $M_w$  in Figure 3. Here, F15, F33, F65 and F110 represent polymacromonomers consisting of side chains with 15, 33, 65 and 113 styrene residues, respectively.  $A_2$  values smaller than 10<sup>-5</sup> cm<sup>3</sup> mol g<sup>-2</sup> were not included in the figure because they are less accurate. It is seen that  $A_2$  decreases with  $M_w$  and that the slope becomes steeper with increasing side-chain length.

These data may be explained by the following equation for the wormlike chain,<sup>27</sup>

$$A_2 = A_2^0 + A_2^{(E)} \quad (22)$$

Here,  $A_2^0$  represents the term without the contribution of the chain-end effect and may be calculated from the following equation for the wormlike chain<sup>21</sup>

$$A_2^0 = \frac{N_A L^2 B}{2M^2} h(\lambda B, \lambda L) \quad (23)$$

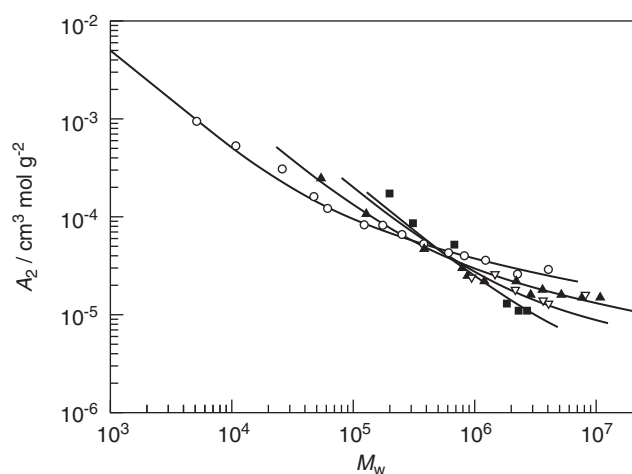
where  $N_A$ ,  $L$  and  $M$  denote the Avogadro constant, the contour length of the polymacromonomer molecule and molecular weight, respectively. The last two parameters can be related by  $L = M/M_L$  with the molecular weight per unit contour length  $M_L$ . The dimensionless variable  $h(\lambda B, \lambda L)$  may be calculated from the modified Barrett equation.<sup>21,27,28</sup>

The term  $A_2^{(E)}$  for the chain-end effects may be expressed as<sup>27</sup>

$$A_2^{(E)} = a_{2,1} M^{-1} + a_{2,2} M^{-2} \quad (24)$$

Here,  $a_{2,1}$  and  $a_{2,2}$  are constants. The second term of the right-hand side of equation (24) is neglected here.

$B$  and  $a_{2,1}$  are determined by fitting calculated curves to the data points as illustrated by the solid lines in Figure 3, where known values of  $\lambda^{-1}$  and  $M_L$  for each sample<sup>12,15,18</sup> were used. The variable  $h_s$  was taken to be 0.26 nm, the averaged value for these samples.<sup>12,15,18</sup> The value  $\beta_2 = 0.034$  nm<sup>3</sup> known for linear PS in toluene at 15.0 °C<sup>29</sup> and  $b = 0.74$  nm calculated from the unperturbed dimension of PS in cyclohexane at 34.5 °C<sup>30</sup> were also used. The value for the highest molecular weight sample of F65 is less accurate because the



**Figure 3** Molecular weight dependence of the second virial coefficient for polystyrene polymacromonomers with different degrees of polymerization of the side chain in toluene: circles, F15;<sup>12</sup> filled triangles, F33;<sup>12</sup> unfilled triangles, F65;<sup>15</sup> squares, F110;<sup>18</sup> lines, calculated values.

measurements were taken at low concentrations, therefore, it was omitted from the fitting. The resulting values are summarized in Table 1.

The circles in Figure 4 show the values of  $B$  thus determined plotted against  $n_s$ . The values obtained from the current analyses are close to those determined from  $\langle S^2 \rangle$  shown by the squares. The dashed line in Figure 4 represents the calculated values from equation (9). It is seen that they are much larger than the experimental values. The calculated values from the SD model represented by the solid line are much closer to the experimental data. This result suggests that the segment distribution around the main chain of polymacromonomer molecules can be described by the Gaussian function even if the conformation of each side chain with small  $n_s$  is far from Gaussian.

### Theta solvent systems

In Table 2, calculated  $B$  values from  $\nu_{2-1}$  and  $\nu_2^{SD}$  according to equations (19) and (21), respectively, are summarized. Here,  $\beta_3 = 0.004$  nm<sup>3</sup> is used, as determined from the third virial coefficients of linear PS in cyclohexane at 34.5 °C.<sup>24</sup> It is seen that the values from the perturbation calculation are much larger than those for the SD model. If we ignore the chain-end effect, the maximum values of  $A_2$  may be calculated from equation (23) with  $h(\lambda B, \lambda L) = 1$ . The  $A_2$  values

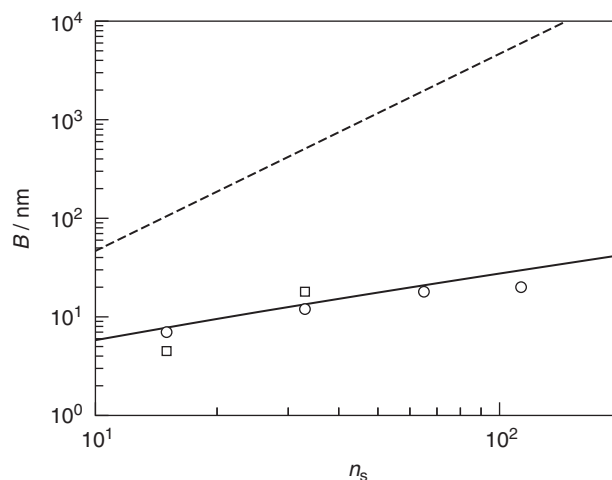
**Table 1** Molecular parameters for polystyrene polymacromonomers in toluene at 15.0 °C

Sample	$n_s$	$M_L$ (10 <sup>3</sup> nm <sup>-1</sup> )	$\lambda^{-1}$ (nm)	$a_{2,1}$ (cm <sup>3</sup> g <sup>-1</sup> )	B (nm)	
					From $\langle S^2 \rangle$	From $A_2$
F15	15	6.2 <sup>a</sup>	16 <sup>a</sup>	5	4.5 <sup>a</sup>	7
F33	33	13.0 <sup>a</sup>	36 <sup>a</sup>	12	18 <sup>a</sup>	12
F65	65	25.0 <sup>b</sup>	75 <sup>b</sup>	20	—	18
F110	113	45.5 <sup>c</sup>	155 <sup>c</sup>	25	—	20

<sup>a</sup>Terao *et al.*<sup>12</sup>

<sup>b</sup>Hokajo *et al.*<sup>15</sup>

<sup>c</sup>Sugiyama *et al.*<sup>18</sup>



**Figure 4**  $B$  for polystyrene polymacromonomers determined from the radius expansion factor (squares)<sup>12</sup> and the second virial coefficient (circles). Dashed and solid lines show calculated values from equation (2) with equations (9) and (12), respectively.

**Table 2** Calculated  $B$  for polystyrene polymacromonomers in cyclohexane at 34.5 °C

$n_s$	$B$ (nm)	
	From $v_{3-2}$	From $v_3^{SD}$
15	55	6
33	268	10
65	1038	15
113	3137	21

obtained with  $B$  based on the SD model were less than  $2 \times 10^{-5} \text{ cm}^3 \text{ mol g}^{-2}$  except for F15. From the previous results, the absolute values of  $A_2$  for PS polymacromonomers in cyclohexane were less than  $3 \times 10^{-5} \text{ cm}^3 \text{ mol g}^{-2}$  at the theta temperature (34.5 °C) irrespective of molecular weight.<sup>11,15,18</sup> Thus, the calculated values for F33, F65 and F110 by the SD model agree with the experimental results. The value for F15 was about  $5 \times 10^{-5} \text{ cm}^3 \text{ mol g}^{-2}$ , which is rather larger than the experimental values.<sup>11</sup> This suggests that it is necessary to consider some other interactions, such as the residual  $\beta_3$  interaction corresponding to the  $n_s^{-1/2}$  term in the square brackets of equation (16), although it cannot be taken into consideration by the SD model. The first-order perturbation calculations gave much larger  $A_2$  values (order of  $10^{-4} \text{ cm}^3 \text{ mol g}^{-2}$ ) than those from the SD model, showing the importance of the closed equation form.

## CONCLUSION

In this study, theoretical investigations of  $B$  for brush-like polymers in good and theta solvents were carried out. It was shown that the SD-model calculations gave closer values to the experimental values in both good and theta solvent systems if binary and ternary interactions among side-chain beads were taken into consideration. The first-order perturbation calculation of  $B$  gave much larger values than the observed ones. This result is similar to the zeroth-order approximation of  $A_2$  for linear flexible polymers.<sup>23</sup> The calculated value for the  $\beta_2^2$  term of  $B$  was much larger than the  $\beta_2$  term, showing that the convergence of the power series in terms of  $\beta_2$  is not good. The  $\beta_2^2$  terms for  $B$  arise from the double interactions between side-chain beads belonging to different brush-like segments. Such higher-order interactions are considered to occur frequently when brush-like segments approach each other in an almost parallel configuration. For the same reason, the SD-model calculation with  $\beta_3$  interactions gave much closer values to the experimental ones for theta solvent systems than the first-order perturbation calculation. However, those values from the SD model calculations still deviate from experimental values by 10–50%. To obtain quantitative agreements, Monte Carlo calculations of  $B$  for the brush-like segments may be desirable.

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- Wintermantel, M., Schmidt, M., Tsukahara, Y., Kajiwara, K. & Kohjiya, S. Rodlike combs. *Macromol. Rapid Commun.* **15**, 279–284 (1994).
- Wintermantel, M., Gerle, M., Fischer, K., Schmidt, M., Wataoka, I., Urakawa, H., Kajiwara, K. & Tsukahara, Y. Molecular bottlebrushes. *Macromolecules* **29**, 978–983 (1996).
- Nakamura, Y. & Norisuye, T. in *Soft Matter Characterization* (eds Borsali, R. & Pecora, R.) Ch 5 (Springer Science+Business Media, LLC, New York, 2008).
- Tsukahara, Y., Ohta, Y. & Senoo, K. Liquid crystal formation of multibranch polystyrene induced by molecular anisotropy associated with its high branch density. *Polymer* **36**, 3413–3416 (1995).
- Wintermantel, M., Fischer, K., Gerle, M., Ries, R., Schmidt, M., Kajiwara, K., Urakawa, H. & Wataoka, I. Lyotropic phases formed by molecular bottlebrushes. *Angew. Chem. Int. Ed. Engl.* **34**, 1472–1474 (1995).
- Nakamura, Y., Koori, M., Li, Y. & Norisuye, T. Lyotropic liquid crystal formation of polystyrene polymacromonomers in dichloromethane. *Polymer* **49**, 4877–4881 (2008).
- Tsukahara, Y., Mizuno, K., Segawa, A. & Yamashita, Y. Study on the radical polymerization behavior of macromonomers. *Macromolecules* **22**, 1546–1552 (1989).
- Tsukahara, Y., Tsutsumi, K., Yamashita, Y. & Shimada, S. Radical polymerization behavior of macromonomers. 2. Comparison of styrene macromonomers having a methacryloyl end group and a vinylbenzyl end group. *Macromolecules* **23**, 5201–5208 (1990).
- Nemoto, N., Nagai, M., Koike, A. & Okada, S. Diffusion and sedimentation studies of poly(macromonomer) in dilute solution. *Macromolecules* **28**, 3854–3859 (1995).
- Kawaguchi, S., Akaike, K., Zhang, Z.-M., Matsumoto, H. & Ito, K. Water soluble bottlebrushes. *Polym. J.* **30**, 1004–1007 (1998).
- Terao, K., Takeo, Y., Tazaki, M., Nakamura, Y. & Norisuye, T. Solution properties of polymacromonomers consisting of polystyrene. Light scattering characterization in cyclohexane. *Polym. J.* **31**, 193–198 (1999).
- Terao, K., Nakamura, Y. & Norisuye, T. Solution properties of polymacromonomers consisting of polystyrene. 2. Chain dimensions and stiffness in cyclohexane and toluene. *Macromolecules* **32**, 711–716 (1999).
- Terao, K., Hokajo, T., Nakamura, Y. & Norisuye, T. Solution properties of polymacromonomers consisting of polystyrene. 3. Viscosity behavior in cyclohexane and toluene. *Macromolecules* **32**, 3690–3694 (1999).
- Zhang, B., Gröhn, F., Pedersen, J. S., Fischer, K. & Schmidt, M. Conformation of cylindrical brushes in solution: effect of side chain length. *Macromolecules* **39**, 8440–8450 (2006).
- Hokajo, T., Terao, K., Nakamura, Y. & Norisuye, T. Solution properties of polymacromonomers consisting of polystyrene. 5. Effect of side chain length on chain stiffness. *Polym. J.* **33**, 481–485 (2001).
- Hokajo, T., Hanaoka, Y., Nakamura, Y. & Norisuye, T. Translational diffusion coefficient of polystyrene polymacromonomers. Dependence on side-chain length. *Polym. J.* **37**, 529–534 (2005).
- Amitani, K., Terao, K., Nakamura, Y. & Norisuye, T. Small-angle X-ray scattering from polystyrene polymacromonomers in cyclohexane. *Polym. J.* **37**, 324–331 (2005).
- Sugiyama, M., Nakamura, Y. & Norisuye, T. Dilute-solution properties of polystyrene polymacromonomer having side chains of over 100 monomeric units. *Polym. J.* **40**, 109–115 (2008).
- Nakamura, Y. & Norisuye, T. Backbone stiffness of comb-branched polymers. *Polym. J.* **33**, 874–878 (2001).
- Yamakawa, H. & Stockmayer, W. H. Statistical mechanics of wormlike chains. II. Excluded volume effects. *J. Chem. Phys.* **57**, 2843–2854 (1972).
- Yamakawa, H. *Helical Wormlike Chains in Polymer Solutions* (Springer, Berlin, 1997).
- Fixman, M. & Skolnick, J. Polyelectrolyte excluded volume paradox. *Macromolecules* **11**, 863–867 (1978).
- Yamakawa, H. *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971).
- Nakamura, Y., Norisuye, T. & Teramoto, A. Second and third virial coefficients for polystyrene in cyclohexane near the  $\Theta$  point. *Macromolecules* **24**, 4904–4908 (1991).
- Wang, M. C. & Uhlenbeck, G. E. On the theory of the brownian motion II. *Rev. Mod. Phys.* **17**, 323–342 (1945).
- Cherayil, B. J., Douglas, J. F. & Freed, K. F. Effect of residual interactions on polymer properties near the theta point. *J. Chem. Phys.* **83**, 5293–5310 (1985).
- Yamakawa, H. On the theory of the second virial coefficient for polymer chains. *Macromolecules* **25**, 1912–1916 (1992).
- Barrett, A. J. Second osmotic virial coefficient for linear excluded volume polymers in the Domb-Joyce model. *Macromolecules* **18**, 196–200 (1985).
- Abe, F., Einaga, Y., Yoshizaki, T. & Yamakawa, H. Excluded-volume effects on the mean-square radius of gyration of oligo- and polystyrenes in dilute solutions. *Macromolecules* **26**, 1884–1890 (1993).
- Miyaki, Y., Einaga, Y. & Fujita, H. Excluded-volume effects in dilute polymer solutions. 7. Very high molecular weight polystyrene in benzene and cyclohexane. *Macromolecules* **11**, 1180–1186 (1978).