

## Remarks on Excluded-Volume Effects in Semiflexible Polymer Solutions

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**ABSTRACT:** Intramolecular excluded-volume effects in stiff chains are examined by analyzing typical data of  $\langle S^2 \rangle$  (the mean-square radius of gyration) and  $[\eta]$  (the intrinsic viscosity) for four different polymers with Kuhn segment lengths  $\lambda^{-1}$  of 7.8–86 nm on the basis of the wormlike chain. The data are shown to be explained almost quantitatively in the Yamakawa–Stockmayer–Shimada scheme for wormlike or helical wormlike chains, leading to the conclusion that the expansion factor versus scaled excluded-volume parameter relations established by Yamakawa, Einaga, and coworkers for  $\langle S^2 \rangle$  and  $[\eta]$  of linear flexible polymers apply to semiflexible chains in a good approximation. For typical stiff chains, the volume effects are negligibly small up to a reduced contour length  $\lambda L$  of 20–50, as was found by Norisuye and Fujita. This substantially unperturbed behavior is due to the fact that the reduced excluded-volume strength  $\lambda B$  for such a chain is one order of magnitude smaller than those for flexible chains in good solvents. It is noted, however, that a stiff chain starts deviating from the unperturbed state at  $\lambda L \sim 3$  when it happens to have a  $\lambda B$  value comparable to those for the latter group.

**KEY WORDS** Excluded-Volume Effect / Stiff Chain / Expansion Factor / Wormlike Chain / Helical Wormlike Chain /

Molecular characterization of semiflexible polymers in dilute solution often requires knowledge of intramolecular excluded-volume effects, but our understanding of those effects in stiff chains still leaves much to be desired. The situation may be explained as follows. More than 10 years ago, Norisuye and Fujita,<sup>1</sup> analyzing available data for the mean-square radius of gyration  $\langle S^2 \rangle$  on the basis of the Kratky–Porod (KP) wormlike chain,<sup>2</sup> concluded that excluded-volume effects on  $\langle S^2 \rangle$  of various polymers become experimentally observable when the Kuhn segment number  $n_k$  exceeds 50 ( $\pm 30$ ). This  $n_k$  value was one order of magnitude larger than that predictable from the Yamakawa–Stockmayer perturbation theory<sup>3</sup> for KP bead chains, suggesting that intramolecular volume exclusion in actual stiff polymers is less enhanced than predicted by the theory. Later, Yamakawa and Shimada<sup>4</sup> examined the discrepancy by directly comparing theoretical and experimental  $\langle S^2 \rangle$  values, and reached the conclusion that the Yamakawa–Stockmayer scheme, now extended to helical wormlike (HW) chains<sup>5</sup> and called the Yamakawa–Stockmayer–Shimada (YSS) scheme, breaks down for poly(hexyl isocyanate) (PHIC), a typical stiff chain, in hexane.<sup>6</sup> Little progress has since been made on the subject, though, as far as flexible polymers are concerned, the validity of the YSS scheme has been substantiated for both dimensional and hydrodynamic properties.<sup>7–12</sup>

Very recently Tsuboi *et al.*<sup>13</sup> analyzed data of  $\langle S^2 \rangle$  and  $[\eta]$  (the intrinsic viscosity) for cellulose tris(3,5-dimethylphenylcarbamate) (CTDC) in 1-methyl-2-pyrrolidone (NMP) to reconcile the YSS theory with Norisuye and Fujita's conclusion mentioned above. The point was that the theory was capable of explaining the observed volume effects that were practically negligible for  $n_k < 40$  and appreciable for  $n_k > 50$ . This motivated us to re-examine literature data of  $\langle S^2 \rangle$  and  $[\eta]$  including those for PHIC with a hope of deepening our understanding of the intramolecular excluded-volume effects in semiflexible polymer solutions. To make our

analysis more quantitative than in the earlier work by Norisuye and Fujita, we here confine ourselves to polymers whose  $\langle S^2 \rangle$  or  $[\eta]$  data show both unperturbed and perturbed behaviors in the molecular weight range studied. They are CTDC in NMP,<sup>13,14</sup> sodium salt of hyaluronic acid (Na-HA) in 0.2 and 0.5 M aqueous sodium chloride,<sup>15–17</sup> and poly(1-phenyl-1-propyne) (PPP) in toluene,<sup>18</sup> in addition to PHIC in hexane.<sup>6</sup> No polyelectrolyte in aqueous solution of low ionic strength is included. According to the characterization studies by previous workers,<sup>6,13–18</sup> all the chosen polymers are modeled well by the KP chain.

### DATA ANALYSIS

#### *Theoretical Relations*

For convenience of our presentation, we first summarize necessary relations appearing in the YSS scheme, confining ourselves to the KP limit of the HW chain. The unperturbed mean-square radius of gyration  $\langle S^2 \rangle_0$  of the KP chain is given by<sup>19</sup>

$$\lambda^2 \langle S^2 \rangle_0 = \frac{\lambda L}{6} - \frac{1}{4} + \frac{1}{4\lambda L} - \frac{1}{8(\lambda L)^2} [1 - \exp(-2\lambda L)] \quad (1)$$

Here,  $\lambda^{-1}$  is the Kuhn segment length (the stiffness parameter in the HW chain) and  $L$  is the contour length. The latter is related to the molecular weight  $M$  by  $M_L = M/L$ , with  $M_L$  being the molar mass per unit contour length of the chain, so that  $\langle S^2 \rangle_0$  of the KP chain is characterized by  $\lambda^{-1}$  and  $M_L$ . The Yamakawa–Fujii–Yoshizaki theory<sup>20,21</sup> for the intrinsic viscosity  $[\eta]_0$  of an unperturbed KP cylinder contains one additional parameter, the cylinder diameter  $d$ . If the Yoshizaki–Nitta–Yamakawa theory<sup>22</sup> based on the touched-bead model is adopted, this hydrodynamic diameter is replaced by the bead diameter  $d_b$ , but the two theories are essentially equivalent.

The YSS theory<sup>3-5</sup> predicts that the radius expansion factor  $\alpha_S \equiv (\langle S^2 \rangle / \langle S^2 \rangle_0)^{1/2}$  and the viscosity expansion factor  $\alpha_\eta \equiv ([\eta] / [\eta]_0)^{1/3}$  are universal functions of the scaled excluded-volume parameter  $\tilde{z}$  defined by

$$\tilde{z} = (3/4)K(\lambda L)z \quad (2)$$

with

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

and

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

Here,  $z$  is the conventional excluded-volume parameter and  $B$  is the excluded-volume strength defined for the KP chain by

$$B = \beta/a^2 \quad (5)$$

with  $\beta$  and  $a$  being the binary cluster integral representing the interaction between a pair of beads and the bead spacing, respectively. The  $K(\lambda L)$  function is essentially zero for  $\lambda L < 1$  due to the stiffness effect and approaches the coil limiting value  $4/3$  in the limit of infinite  $\lambda L$ . Thus,  $\tilde{z}$  is identical to  $z$  in the coil limit.

The Domb-Barrett function<sup>23</sup> and the Barrett function<sup>24</sup> are usually adopted for  $\alpha_S^2$  and  $\alpha_\eta^3$ , respectively. In the YSS scheme, they read<sup>4,9</sup>

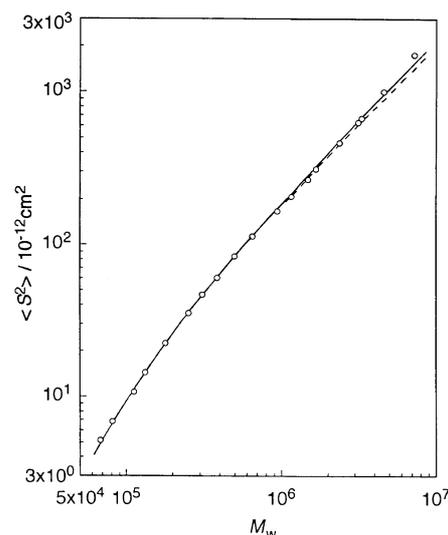
$$\alpha_S^2 = \left[ 1 + 10\tilde{z} + \left( \frac{70\pi}{9} + \frac{10}{3} \right) \tilde{z}^2 + 8\pi^{3/2} \tilde{z}^3 \right]^{2/15} \times [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \quad (6)$$

$$\alpha_\eta^3 = (1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.3} \quad (7)$$

These equations accurately describe experimental data for flexible polymers with  $\lambda^{-1}$  of 1.3–5.8 nm over a very broad range of molecular weight.<sup>8-12</sup> Equations 2 through 7 indicate that  $B$  needs to be known (in addition to the model parameters characterizing the unperturbed KP chain) in order to evaluate the theoretical  $\alpha_S^2$  and  $\alpha_\eta^3$  and hence the theoretical  $\langle S^2 \rangle$  and  $[\eta]$  in the perturbed state.

#### Re-analysis of PHIC Data

As mentioned in the Introduction, the dimensional data of PHIC have been a matter of discussion. For this polymer (in hexane at 25°C), Murakami *et al.*<sup>6</sup> obtained  $\lambda^{-1} = 84 \pm 2$  nm and  $M_L = 715 \pm 15$  nm<sup>-1</sup> from  $\langle S^2 \rangle$  data covering a broad range of weight-average molecular weight  $M_w$  from  $7 \times 10^4$  to  $7 \times 10^6$ , and showed that these parameter values within the indicated uncertainties allow the measured  $\langle S^2 \rangle$  and scattering functions for fractions with  $M_w < 1.7 \times 10^6$  to be described quite accurately by the known theories for the unperturbed KP chains. These authors also found a good agreement between their  $[\eta]$  data and the theoretical  $[\eta]_0$  values for the KP cylinder with  $\lambda^{-1} = 84$  nm,  $M_L = 715$  nm<sup>-1</sup>, and  $d = 1.6$  nm in the region of  $M_w$  below  $4 \times 10^6$ . Thus any  $\lambda^{-1}$  and  $M_L$  values outside the indicated uncertainties seem irrelevant. In their analysis of the  $\langle S^2 \rangle$  data mentioned in the Introduction, Yamakawa and

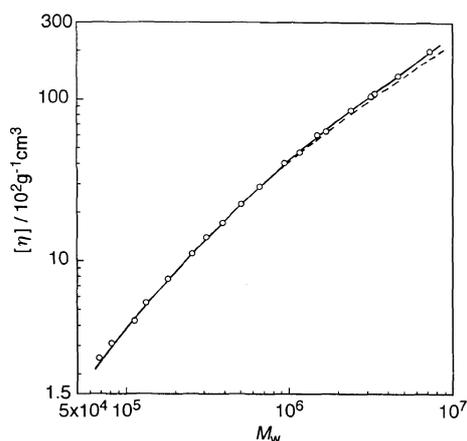


**Figure 1.** Re-analysis of the  $\langle S^2 \rangle$  data of Murakami *et al.*<sup>6</sup> for PHIC in hexane at 25°C. Solid line, theoretical values calculated from eq 1 and 6 for the perturbed KP chain with  $\lambda^{-1} = 86$  nm,  $M_L = 730$  nm<sup>-1</sup>, and  $B = 2.6$  nm; dashed line, theoretical values for the unperturbed KP chain ( $B = 0$ ).

Shimada<sup>4</sup> fixed  $\lambda^{-1}$  and  $M_L$  to 84 nm and 715 nm<sup>-1</sup>, respectively, *i.e.*, to the values of Murakami *et al.* We here allow  $\lambda^{-1}$  and  $M_L$  to take any values within the above uncertainties (*i.e.*,  $\pm 2$  nm for  $\lambda^{-1}$  and  $\pm 15$  nm<sup>-1</sup> for  $M_L$ ), and examine whether there is a set of parameters giving a reasonably good agreement between theory and experiment for each of  $[\eta]$  and  $\langle S^2 \rangle$  when excluded-volume effects are taken into account according to eq 6 and 7. It may be anticipated that since intramolecular excluded-volume effects in stiff chains are generally small, their evaluation is very sensitive to the estimated values of  $\lambda^{-1}$  and  $M_L$ .

Figure 1 compares the  $\langle S^2 \rangle$  data of Murakami *et al.*<sup>6</sup> for PHIC with the solid curve calculated from eq 1 and 6 for  $\lambda^{-1} = 86$  nm,  $M_L = 730$  nm<sup>-1</sup>, and  $B = 2.6$  nm, where the dashed line represents the theoretical  $\langle S^2 \rangle_0$  values. One data point at the highest  $M_w$  deviates appreciably from the solid curve, but the general agreement is not bad. The data points are somewhat better fitted by the dashed line for  $M_w$  between  $9 \times 10^5$  and  $3 \times 10^6$  and go up beyond the solid line for  $M_w$  above  $4 \times 10^6$ , as was found by Yamakawa and Shimada<sup>4</sup> who used a similar parameter set ( $\lambda^{-1} = 84$  nm,  $M_L = 715$  nm<sup>-1</sup>, and  $B = 2.52$  nm). Such sudden departure of the data points from the dashed line at  $M_w \sim 3 \times 10^6$ , *i.e.*,  $\lambda L (= n_K) \sim 50$ , was previously<sup>1,4</sup> taken to show certain shortcomings of the YSS scheme. However, it is probably fair to say that the deviation of the data points (except at the highest  $M_w$ ) from the YSS theoretical curve (the solid line) is hardly beyond experimental error.

Figure 2 shows that the molecular weight dependence of  $[\eta]$  for the same system is described accurately by the Yamakawa-Fujii-Yoshizaki theory<sup>20,21</sup> with eq 7 for  $\lambda^{-1} = 82$  nm,  $M_L = 730$  nm<sup>-1</sup>,  $d = 1.8$  nm, and  $B = 2.6$  nm throughout the entire range of molecular weight studied. The agreement is much more satisfactory than that for  $\langle S^2 \rangle$ . The dashed line, which again refers to the unperturbed state, fits the data points up to  $M_w \sim 2 \times 10^6$ .



**Figure 2.** Re-analysis of the  $[\eta]$  data of Murakami *et al.*<sup>6</sup> for PHIC in hexane at 25°C. Solid line, theoretical values calculated from the Yamakawa–Fujii–Yoshizaki theory<sup>20,21</sup> and eq 7 for the perturbed KP chain with  $\lambda^{-1}=82$  nm,  $M_L=730$  nm<sup>-1</sup>,  $d=1.8$  nm, and  $B=2.6$  nm; dashed line, theoretical values for the unperturbed KP chain.

The unperturbed line shown by Murakami *et al.* for  $\lambda^{-1}=84$  nm,  $M_L=715$  nm<sup>-1</sup>, and  $d=1.6$  nm (Figure 15 in ref 6) is close to our perturbed line (the solid curve) for  $M_w < 4 \times 10^6$  rather than the dashed line in Figure 2, showing that a slight alteration in parameter set considerably affects the estimation of excluded-volume effects. The present  $\lambda^{-1}$  value of 82 nm chosen for  $[\eta]$  is 5% smaller than that (86 nm) used for the above analysis of  $\langle S^2 \rangle$  data, but the difference seems plausible since the  $z$ -average to weight-average molecular weight ratios ( $M_z/M_w$ ) reported by Murakami *et al.* for several PHIC fractions are 1.05. In short, we may say that the PHIC data do not definitely show the YSS theory to have serious shortcomings.

#### Model Parameters and Onset of Volume Effect

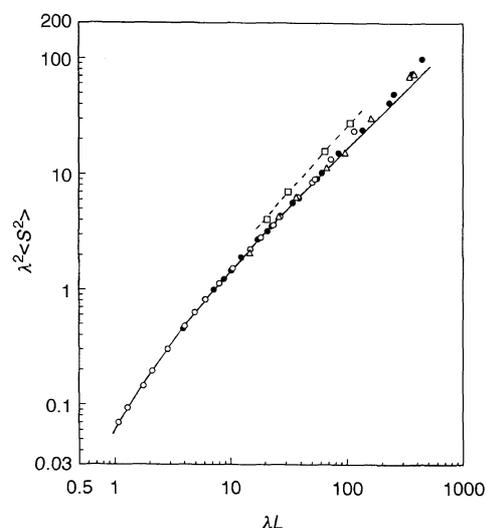
The values of  $\lambda^{-1}$ ,  $M_L$ ,  $d$ , and  $B$  estimated above for PHIC in hexane are summarized in Table I, in which those recently reported for CTDC in NMP,<sup>13</sup> Na-HA in 0.2 and 0.5 aqueous NaCl,<sup>17</sup> and PPP in toluene<sup>18</sup> are included. For the last polymer, a theta solvent (cyclohexane at 36°C) is available, and  $\langle S^2 \rangle_\theta$  in it (the subscript  $\theta$  signifies the theta state) agrees with  $\langle S^2 \rangle$  of the same sample in toluene within experimental error for  $M_w \leq 10^5$ .<sup>18</sup> Hence,  $\alpha_S^2$  for PPP in the latter solvent may be obtained directly from the ratio of  $\langle S^2 \rangle$  to  $\langle S^2 \rangle_\theta$ . The  $B$  value of 0.43 nm for this polymer in the table has been estimated in this work by comparing the  $\alpha_S^2$  data for several higher molecular weight fractions with eq 6. This  $B$  value is the smallest among those for the four stiff chains but comparable to the reported values for typical flexible polymer + good solvent systems such as polystyrene in toluene (0.61 nm)<sup>8</sup> and polyisobutylene in cyclohexane (0.31 nm).<sup>25</sup> Another point to note in the table is that the  $\lambda^{-1}$  values for Na-HA in 0.2 and 0.5 M aqueous NaCl are essentially the same and thus indicate negligible contributions from electrostatic interactions between groups to the chain stiffness.

Figure 3 shows the plots of  $\lambda^2 \langle S^2 \rangle$  vs.  $\lambda L$  constructed from the reported  $\langle S^2 \rangle$  data for the four polymers<sup>6,13,14,17,18</sup> and the values of  $\lambda^{-1}$  and  $M_L$  in Table I; the  $\langle S^2 \rangle$  data for PHIC have been reproduced from Figure 1, and those for Na-HA (in 0.5 M aqueous NaCl)

**Table I.** Model parameters characterizing semiflexible polymers in the unperturbed and perturbed states

Polymer	Solvent (25°C)	Property	$\lambda^{-1}$	$M_L$	$d$	$B$	$\lambda B$
			nm	nm <sup>-1</sup>	nm	nm	
PHIC <sup>a</sup>	Hexane	$\langle S^2 \rangle$	86	730	2.6	0.030	
		$[\eta]$	82	730	1.8	0.032	
CTDC <sup>b</sup>	NMP	$\langle S^2 \rangle$	15.6	1080	0.50	0.032	
		$[\eta]$	15.6	1140	3.9 <sup>f</sup>	0.50	0.032
Na-HA <sup>c</sup>	0.2 M NaCl	$[\eta]$	8.4	405	1.0	3.4	0.41
	0.5 M NaCl	$\langle S^2 \rangle$ & $[\eta]$	8.2	400	1.0	2.8	0.34
PPP <sup>d</sup>	Toluene	$\langle S^2 \rangle$ & $[\eta]$ <sup>e</sup>	7.8	490	1.1	0.43	0.055

<sup>a</sup> Poly(hexyl isocyanate) (ref 6). <sup>b</sup> Cellulose tris(3,5-dimethylphenyl-carbamate) (refs 13, 14). <sup>c</sup> Sodium salt of hyaluronic acid (refs 15–17). All the model parameters in the two aqueous salts were determined from  $[\eta]$  data in ref 17. <sup>d</sup> Poly(1-phenyl-1-propyne) (ref 18). <sup>e</sup> Flory viscosity factor in the unperturbed coil limit is taken as  $2.35 \times 10^{23}$  mol<sup>-1</sup>. <sup>f</sup> Bead diameter.



**Figure 3.** Plots of  $\log \lambda^2 \langle S^2 \rangle$  vs.  $\log \lambda L$  constructed from reported  $\langle S^2 \rangle$  data for PHIC in hexane (○),<sup>6</sup> CTDC in NMP (●),<sup>13,14</sup> Na-HA in 0.5 M aqueous NaCl (□),<sup>17</sup> and PPP in toluene (△).<sup>18</sup> Solid line, eq 1; dashed line, empirical fit to the Na-HA data.

and PPP (in toluene) have been corrected for polydispersity with  $M_z/M_w=1.10$  for the former<sup>17</sup> and  $M_z/M_w=1.07$  for the latter<sup>18</sup> since both  $\lambda^{-1}$  and  $M_L$  for the polymers in the table refer to the “monodisperse” values. The solid curve represents eq 1 for the unperturbed KP chain. It can be seen that except for Na-HA, the plotted points start deviating upward from this unperturbed line at a  $\lambda L (=n_k)$  of 20–50. This finding is consistent with Norisuye and Fujita’s conclusion (on stiff chains) mentioned in the Introduction. However, their conclusion does not apply to Na-HA, whose data deviate considerably upward from the solid curve even at  $\lambda L=20$ . As shown by Hayashi *et al.*,<sup>17</sup> extensive  $[\eta]$  data for this polysaccharide in either 0.2 or 0.5 M aqueous NaCl are in line with this observation and start deviating from  $[\eta]_0$  (for the KP cylinders with the parameter values in Table I) at  $\lambda L \sim 3$ . This critical  $\lambda L$  value for the onset of volume effect is close to those usually observed for flexible polymers in good solvents.

The  $\lambda^{-1}$  values for Na-HA in both 0.2 and 0.5 M aqueous NaCl are much smaller than those for PHIC and CTDC but comparable to that for PPP (see Table

I), so that the weak stiffness of the polysaccharide chain is not directly responsible for the observed volume effects at  $\lambda L$  smaller than 20. As the last column of Table I shows, the values of  $\lambda B$  for Na-HA in the two aqueous salts are one order of magnitude larger than those for the other stiff chains. Thus, these large  $\lambda B$  values must be responsible for the excluded-volume behavior of the Na-HA chain seemingly different from that of the other stiff polymers. Interestingly, they are comparable to most of the reported  $\lambda B$  values<sup>7-12,25,26</sup> (0.2–0.6) for flexible polymers in good solvents, being consistent with the finding<sup>17</sup> that the Na-HA chain starts deviating from the unperturbed state at  $\lambda L \sim 3$  as if it were a flexible chain.

In conclusion, we find that the magnitude of  $\lambda B$  relates to the experimental observations of the onset of volume effect in stiff chains when the contour length is expressed in units of  $\lambda^{-1}$ . This was overlooked in the earlier work.<sup>1</sup> It should be noted, however, that for  $\lambda L$  below 20–50, volume effects on  $\langle S^2 \rangle$  and  $[\eta]$  of typical stiff chains with  $\lambda B < 0.05$  are hardly observable and may be ignored for the practical purpose of estimating  $\lambda^{-1}$  and  $M_L$ , if any.

### EXPANSION FACTORS

Radius expansion factors may be obtained from the experimental  $\langle S^2 \rangle$  values (in Figure 3) relative to the theoretical unperturbed values (eq 1) as functions of  $\tilde{z}$  if the values of  $\lambda^{-1}$ ,  $M_L$ , and  $B$  for the respective systems in Table I are used; as noted above, the directly measured  $\alpha_S^2$  data can be used for PPP. The resulting plots of  $\alpha_S^2$  vs.  $\log \tilde{z}$  for the four semiflexible polymers are shown in Figure 4, in which the curve represents eq 6. The plotted points come fairly close to this curve, showing that the YSS scheme for  $\alpha_S^2$  is a good approximation to the polymer + solvent systems examined here. In this connection, two remarks may be pertinent here.

First, the agreement in the region of  $\tilde{z}$  below 0.02, where  $\alpha_S^2 < 1.02$ , is no other than that between the measured  $\langle S^2 \rangle$  and the theoretical values for the unperturbed KP chain, but its implication is that the YSS theory properly scales the excluded-volume parameter to give  $\alpha_S^2 \sim 1$  in the associated chain length region. Second, most data points continue staying at about unity up to  $\tilde{z} \sim 0.05$ , manifesting the finding in Figure 3 that except for Na-HA, the  $\langle S^2 \rangle$  values for  $\lambda L$  below 20–50 are substantially unperturbed by excluded-volume effect. Though the theoretical curve in Figure 4 gradually rises in the region of  $\tilde{z}$  between 0.02 and 0.05, the discrepancy between theory and experiment is at most 6% in that region and hence cannot be considered serious.

Figure 5 shows the plots of  $\alpha_\eta^3$  vs.  $\log \tilde{z}$  constructed for the four semiflexible polymers with the reported data<sup>6,13-18</sup> for  $[\eta]$  and the parameter values in Table I. The necessary values of  $[\eta]_0$  for the respective polymers have been computed from the Yamakawa–Fujii–Yoshizaki theory<sup>20,21</sup> for KP cylinders (for PHIC, Na-HA, and PPP) or the Yoshizaki–Nitta–Yamakawa theory<sup>22</sup> for KP touched-bead chains (for CTDC); the  $[\eta]_0$  values for PPP in cyclohexane at 36°C were not used, since Hirao *et al.*<sup>18</sup> found a subtle difference in

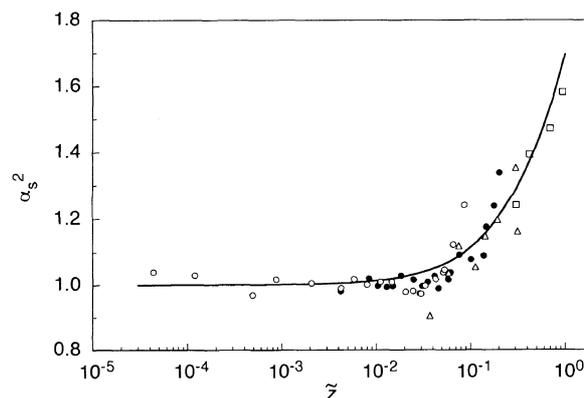


Figure 4. Comparison between experimental  $\alpha_S^2$  and eq 6 (the solid line). The symbols are the same as those used in Figure 3.

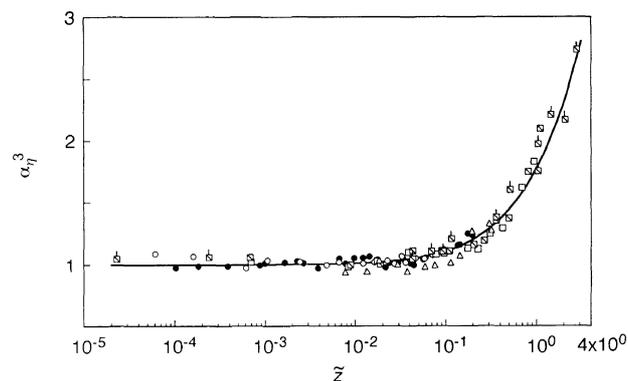


Figure 5. Comparison between experimental  $\alpha_\eta^3$  and eq 7 (the solid line). The symbols are the same as those used in Figure 4, but the data of Hayashi *et al.*<sup>17</sup> ( $\square$ ) and Cleland and Wang<sup>15,16</sup> ( $\boxtimes$ ) for Na-HA in 0.2M aqueous NaCl are added.

$\Phi_{0\infty}$  (Flory's viscosity factor in the unperturbed coil limit) between toluene and cyclohexane (in the calculation of  $[\eta]_0$  in toluene,  $\Phi_{0\infty}$  was taken to be  $2.35 \times 10^{23} \text{ mol}^{-1}$  instead of  $2.87 \times 10^{23} \text{ mol}^{-1}$ ). All the plotted points fall on a single curve, demonstrating that at least for the four semiflexible polymers,  $\alpha_\eta^3$  is a function only of  $\tilde{z}$  as required by the YSS theory. This curve actually represents eq 7, and hence its close fit to the data points substantiates that the excluded-volume effects on  $[\eta]$  can be explained almost quantitatively in the YSS scheme.

As already mentioned, the curves in Figures 4 and 5 give close fits to  $\alpha_S^2$  and  $\alpha_\eta^3$  data for flexible polymers over a very wide range of molecular weight. Hence, they can be regarded as essentially universal relations representing the excluded-volume effects on  $\langle S^2 \rangle$  and  $[\eta]$  of linear polymers, flexible and stiff.

### CONCLUSIONS

Excluded-volume effects on  $\langle S^2 \rangle$  and  $[\eta]$  of stiff chains are explained satisfactorily in the framework of the Yamakawa–Stockmayer–Shimada (YSS) theory<sup>3-5</sup> for wormlike or helical wormlike chains, as is the case for flexible polymers. This theory predicts the volume effects to appear at a Kuhn segment number or reduced contour length  $\lambda L$  of about 3, but  $\alpha_S^2$  and  $\alpha_\eta^3$  for typical stiff chains remain close to unity up to a  $\lambda L$  of 20–50. This behavior of the expansion factors is explained in

the YSS scheme by the fact that the values of  $\lambda B$  (the reduced excluded-volume strength) for such chains are one order of magnitude smaller than the reported values for flexible polymers in good solvents. The finding that the sodium hyaluronate chain in 0.2 or 0.5 M aqueous NaCl starts deviating from the unperturbed state at  $\lambda L \sim 3$  can be ascribed to its  $\lambda B$  which happens to be as large as those for flexible chains in good solvents. In any case, the YSS scheme is capable of almost quantitatively predicting the intramolecular excluded-volume effects in linear polymer chains regardless of chain stiffness.

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