

## Translational Diffusion Coefficient of Polystyrene Polymacromonomers. Dependence on Side-Chain Length

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**ABSTRACT:** Dynamic light scattering measurements have been made on two series of polymacromonomer samples consisting of polystyrene with 33 styrene side-chain residues (F33) in cyclohexane at 34.5 °C (a theta solvent) and with 65 styrene side-chain residues (F65) in cyclohexane at 34.5 °C and toluene at 15 °C (a good solvent) to determine the translational diffusion coefficient  $D$  as functions of the weight-average degree of polymerization of the main chain,  $N_w$ , ranging from 15 to 3030 for F33 and from 42 to 1250 for F65. The  $D$  data are compared with those previously obtained for a polystyrene polymacromonomer with a shorter side chain length of 15 styrene residues. The hydrodynamic radius  $R_H$  at fixed  $N_w$  is larger for a longer side-chain polymer and in toluene than in cyclohexane (for F65), reflecting the higher backbone stiffness for the longer side chain and in the good solvent. The  $N_w$ -dependence of  $R_H$  and that of the reduced hydrodynamic radius (the ratio of  $R_H$  to the radius of gyration  $\langle S^2 \rangle^{1/2}$ ) for the respective polymacromonomers are fitted by the theoretical curves for the wormlike chain with the model parameters leading to fits of previous data for the intrinsic viscosity ( $[\eta]$ ) and  $\langle S^2 \rangle$ , provided that the chain diameters  $d$  are taken to be 1.29–1.35 times those from  $[\eta]$ . This discrepancy in  $d$  is similar to what was found for thin stiff chains, revealing certain shortcomings of the current hydrodynamic theories. It is pointed out that polystyrene polymacromonomers with large diameters relative to Kuhn's segment length are hydrodynamically similar to flexible chains for which the available theories for  $D$  contain an error of about 15% in the Gaussian-chain limit. [DOI 10.1295/polymj.37.529]

**KEY WORDS** Polymacromonomer / Dynamic Light Scattering / Translational Diffusion Coefficient / Hydrodynamic Radius / Wormlike Chain / Chain Stiffness / Theta Solvent /

It has been shown in the last one decade that polymacromonomers, regular comb polymers with dense side chains, behave like stiff chains in dilute solution despite being composed of flexible chain units.<sup>1–6</sup> This stiffening effect of side chains ought to be explained in terms of intramolecular interactions between or among monomeric units. To this end, unequivocal determination of the relationships between the backbone stiffness and the side chain length and between the backbone stiffness and the excluded-volume strength is essential, but even systematic data for statistical and hydrodynamic properties are yet insufficient. Notably, Wintermantel *et al.*<sup>1</sup> remarked that measured radii of gyration  $\langle S^2 \rangle$  and intrinsic viscosities  $[\eta]$  for a polymacromonomer consisting of the poly(methyl methacrylate) (PMMA) main chain and polystyrene (PS) side chains in toluene, a good solvent, were not consistently explained by the unperturbed wormlike chain,<sup>7</sup> a typical model for stiff polymers.

Recently, we investigated polymacromonomers F15, F33, and F65 consisting only of PS with 15, 33, and 65 side chain residues, respectively, in cyclohexane at 34.5 °C (a theta solvent) and in toluene at 15 °C

(a good solvent).<sup>8–12</sup> In contrast to the remark by Wintermantel *et al.*,<sup>1</sup> our data of light scattering  $\langle S^2 \rangle$ <sup>8,9,12</sup> and  $[\eta]$ <sup>10,12</sup> for the three polystyrene polymacromonomers were explained consistently by the current theories<sup>13</sup> for the wormlike chain with or without excluded volume when the contribution from side chains near the main-chain ends to the polymacromonomer contour length was taken into consideration. We found from dynamic light scattering (DLS) measurements,<sup>11</sup> however, that the model parameters allowing a close fit to data of the translational diffusion coefficient  $D$  for F15 samples in cyclohexane at 34.5 °C disagreed with those from  $\langle S^2 \rangle$  and  $[\eta]$ . The difference in each parameter was not so large to impair the applicability of the wormlike chain to the polymacromonomer contour and was tentatively attributed to either our simple treatment of the side-chain effect near the main-chain ends or certain shortcomings of the theories<sup>13</sup> for polymer hydrodynamics. Our more recent study<sup>14</sup> on this polymacromonomer by small-angle X-ray scattering showed that the wormlike chain model with this side-chain effect is capable of quantitatively describing experimental  $\langle S^2 \rangle$  and scattering functions in the

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**Table I.** Results from dynamic light scattering measurements on samples of polystyrene polymacromonomers F33 and F65

Sample	Solvent	$M_w/10^4$	$D/10^{-7} \text{ cm}^2\text{s}^{-1}$	$\langle S^2 \rangle^{1/2}/\text{nm}$	$\rho^{-1}$
F33-1		1080 <sup>a</sup>	0.700	54.5 <sup>a</sup>	0.77
F33-2		765 <sup>a</sup>	0.892	44.9 <sup>a</sup>	0.74
F33-3b		598	1.02	37.1	0.78
F33-4		362 <sup>a</sup>	1.25	30.3 <sup>a</sup>	0.78
F33-5	Cyclohexane	289 <sup>a</sup>	1.44	—	—
F33-6	at 34.5 °C	220 <sup>a</sup>	1.61	22.8 <sup>a</sup>	0.80
F33-8		87.3 <sup>a</sup>	2.53	—	—
F33-10		38.4 <sup>a</sup>	3.65	—	—
F33-13		12.8 <sup>a</sup>	5.52	—	—
F33-14		5.43 <sup>a</sup>	7.58	—	—
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F65-1		855 <sup>b</sup>	0.933	40.9 <sup>b</sup>	0.77
F65-2		423 <sup>b</sup>	1.23	28.1 <sup>b</sup>	0.85
F65-3		364 <sup>b</sup>	1.45	25.3 <sup>b</sup>	0.80
F65-4	Cyclohexane	209 <sup>b</sup>	1.74	16.9 <sup>b</sup>	1.06
F65-5	at 34.5 °C	145 <sup>b</sup>	2.16	12.8 <sup>b</sup>	1.06
F65-6		94.3 <sup>b</sup>	2.66	—	—
F65-7		28.6 <sup>b</sup>	3.87	—	—
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F65-1		816 <sup>b</sup>	0.840	54.5 <sup>b</sup>	0.74
F65-2		406 <sup>b</sup>	1.22	35.6 <sup>b</sup>	0.78
F65-3		366 <sup>b</sup>	1.37	30.0 <sup>b</sup>	0.82
F65-4	Toluene	216 <sup>b</sup>	1.77	19.8 <sup>b</sup>	0.97
F65-5	at 15 °C	147 <sup>b</sup>	2.23	14.8 <sup>b</sup>	1.03
F65-6		94.3 <sup>b</sup>	2.71	—	—
F65-7		28.6 <sup>b</sup>	3.90	—	—

<sup>a</sup>from ref 8 and 9, <sup>b</sup>from ref 12

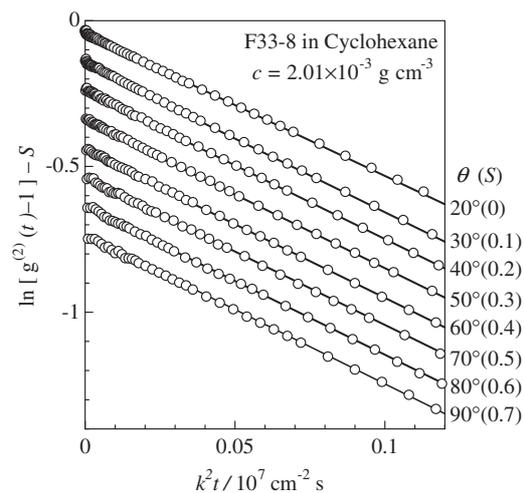
theta solvent down to a very low molecular weight. Thus, the basic theory for  $D$  (or the translational friction coefficient) should be the issue rather than the model itself. Although  $D$  (or the sedimentation coefficient) has extensively been investigated for thin stiff polymers,<sup>15</sup> its well-documented studies for stiff but thick polymers are yet limited to the F15 and PMMA-PS polymacromonomers.<sup>1,2</sup>

In the present work, we extended the DLS study to polymacromonomers F33 and F65 of longer side chains in cyclohexane at 34.5 °C and F65 in toluene at 15 °C to see whether  $D$  data are explained by the available theories with the same model parameters as those describing  $\langle S^2 \rangle$  and  $[\eta]$ . The experimental results and their analysis are presented below.

## EXPERIMENTAL

### Polymacromonomer Samples

The previously investigated samples<sup>8,9</sup> F33-1, F33-2, F33-4, F33-5, F33-6, F33-8, F33-10, F33-13, and F33-14 of polymacromonomer F33 and samples<sup>12</sup> F65-1, F65-2, F65-3, F65-4, F65-5, F65-6, and F65-7 of polymacromonomer F65 were chosen for the present work. To these was added one sample (designated below as F33-3b), which was obtained by frac-



**Figure 1.** Plots of  $\ln[g^{(2)}(t) - 1]$  against  $k^2t$  for polystyrene polymacromonomer sample F33-8 in cyclohexane (34.5 °C) at  $c = 2.01 \times 10^{-3} \text{ g cm}^{-3}$ . The ordinate values at a given scattering angle  $\theta$  are shifted by  $-S$ .

tionation of the previous F33-3 sample. The weight-average molecular weight  $M_w$  of F33-3b was determined to be  $5.98 \times 10^6$  by static light scattering in cyclohexane at 34.5 °C. Weight-average molecular weights for all samples are summarized in the third column of Table I. We note that most of these samples are sufficiently narrow in molecular weight distribution (see ref 8, 9, and 12).

### Dynamic Light Scattering

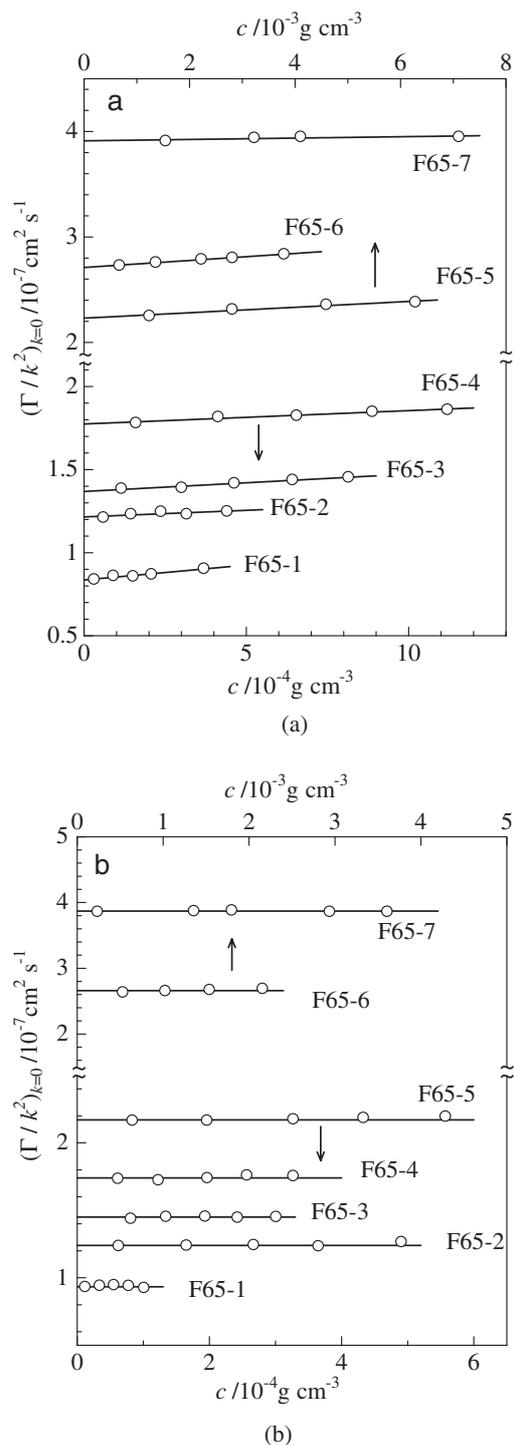
The autocorrelation function  $g^{(2)}(t)$  at time  $t$  was determined at scattering angles  $\theta$  between 20 and 90° for cyclohexane solutions of the F33 samples and cyclohexane and toluene solutions of the F65 samples with different polymer mass concentrations  $c$  using an ALV/DLS/SLS-5000 light-scattering photometer with an ALV-5000E correlator equipped with a YAG laser of 532 nm in wavelength  $\lambda_0$ . The (experimental) first cumulant  $\Gamma$  was evaluated from  $g^{(2)}(t)$  according to the equation

$$\ln[g^{(2)}(t) - 1] = \text{const.} - 2\Gamma t + o(t^2) \quad (1)$$

The desired diffusion coefficient is equal to the infinite dilution value of  $(\Gamma/k^2)_{k=0}$ , *i.e.*,  $\Gamma/k^2$  at  $k = 0$ . Here,  $k$  denotes the magnitude of the scattering vector defined by  $k = (4\pi n_0/\lambda_0) \sin(\theta/2)$  with  $n_0$  being the solvent refractive index.

## RESULTS

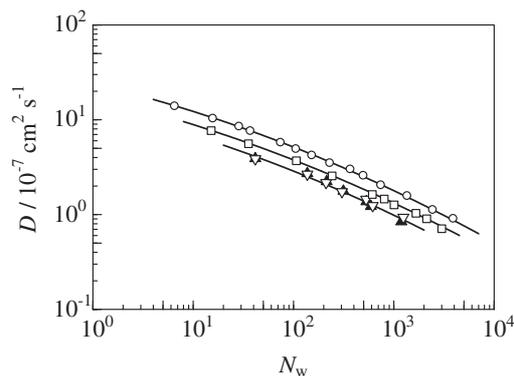
Figure 1 illustrates plots of  $\ln[g^{(2)}(t) - 1]$  against  $k^2t$  at fixed scattering angles for a cyclohexane solution of polymacromonomer sample F33-8 with  $c = 2.01 \times 10^{-3} \text{ g cm}^{-3}$  at 34.5 °C. The data points for the respective angles at  $k^2t < 1 \times 10^6 \text{ s cm}^{-2}$  follow



**Figure 2.** Concentration dependence of  $(\Gamma/k^2)_{k=0}$  for F65 samples in toluene at 15 °C (a) and in cyclohexane at 34.5 °C (b).

straight lines, whose slopes equal  $2\Gamma/k^2$ . Since the slopes are essentially the same, we readily get  $(\Gamma/k^2)_{k=0}$  at this particular polymer concentration of  $2.01 \times 10^{-3} \text{ g cm}^{-3}$ .

The concentration dependence of  $(\Gamma/k^2)_{k=0}$  for toluene and cyclohexane solutions of F65 is shown in Figures 2a and 2b, respectively. The plotted points for each sample in either figure are fitted by a straight line, whose intercept is equal to the desired  $D$ . The



**Figure 3.** Translational diffusion coefficients for polymacromonomers F15 (circles),<sup>11</sup> F33 (squares), and F65 (unfilled triangles) in cyclohexane at 34.5 °C and F65 in toluene at 15 °C (filled triangles) plotted against  $N_w$  (the weight-average degree of polymerization of the main chain). The lines are eye guides.

slopes of the lines for the toluene solutions are all positive, while those for the cyclohexane solutions are essentially zero. The F33 polymacromonomer in cyclohexane exhibited similar concentration dependence. The data of  $D$  thus obtained for all the samples are summarized in Table I, along with our previous  $\langle S^2 \rangle$  data<sup>8,9,12</sup> from static light scattering and the present data for sample F33-3b in cyclohexane.

The  $D$  data for the respective polymacromonomers are plotted double-logarithmically against  $N_w$  (the weight-average degree of polymerization of the main chain) in Figure 3, in which our previous data<sup>11</sup> for polymacromonomer F15 in cyclohexane at 34.5 °C are included for comparison;  $N_w$  is evaluated as  $M_w$  divided by the molecular weight of each macromonomer  $M_0$  (1,650, 3,560, and 6,870 for F15, F33, and F65, respectively). It can be seen that  $D$  in cyclohexane decreases with increasing side chain length when compared at the same  $N_w$ . The  $D$  values for F65 in toluene happen to be close to those in cyclohexane. This is probably because the effect of larger chain dimensions (or higher backbone stiffness) on  $D$  in toluene is offset by the opposite effect of the lower solvent viscosity.

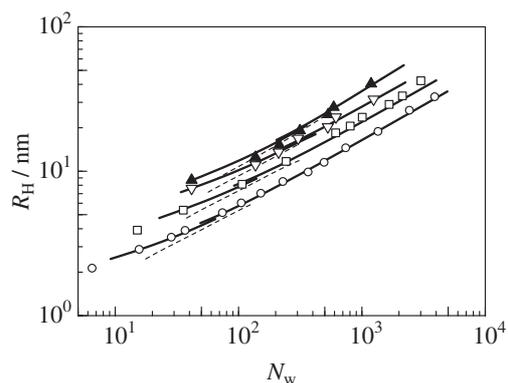
## DISCUSSION

### Hydrodynamic Radius

The hydrodynamic radius  $R_H$  defined by

$$R_H = k_B T / 6\pi\eta_0 D \quad (2)$$

was calculated from the  $D$  data for the three polystyrene polymacromonomers as functions of  $N_w$ , where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\eta_0$  is the solvent viscosity. The resulting  $\log R_H$  vs.  $\log N_w$  relations are illustrated in Figure 4. The relation for each polymer in cyclohexane (the theta



**Figure 4.** Hydrodynamic radii for polycromonomers F15,<sup>11</sup> F33, and F65 in cyclohexane at 34.5 °C and F65 in toluene at 15 °C plotted against  $N_w$ . The symbols are the same as those used in Figure 3. Solid lines: theoretical values from eqs 3 and 4 with the parameters given in Table II; dashed lines: theoretical values for  $\delta = 0$ .

state) is linear with a slope of about 0.5 in the region of  $N_w$  larger than 100, while that for F65 in the good solvent toluene has a slightly higher slope of 0.56 for  $N_w > 200$ . These exponents are close to those known for flexible polymers in theta and good solvents.<sup>13</sup>

The Yamakawa–Fujii theory<sup>16</sup> for the translational friction coefficient of an unperturbed wormlike cylinder may be expressed in terms of  $R_H$  by

$$\begin{aligned}
 R_H^{-1} &= \frac{2}{L} [C_1 \ln \sigma + C_2 + C_3(\lambda L) \\
 &\quad + C_4(\lambda L)^2 + C_5(\lambda L)^3 + C_6 \sigma^{-1} \ln \sigma \\
 &\quad + C_7 \sigma^{-1} + C_8 \sigma^{-2} + C_9 \sigma^{-3} + C_{10} \sigma^{-4}] \\
 &\quad \text{for } \lambda L \leq 2.278 \quad (3) \\
 &= \frac{2}{L} [A_1(\lambda L)^{1/2} + A_2 + A_3(\lambda L)^{-1/2} \\
 &\quad + A_4(\lambda L)^{-1} + A_5(\lambda L)^{-3/2}] \\
 &\quad \text{for } \lambda L > 2.278
 \end{aligned}$$

Here,  $L$  is the contour length of the cylinder,  $\lambda^{-1}$  is the Kuhn segment length,  $\sigma$  is the ratio of  $L$  to the cylinder diameter  $d$ , and the coefficients  $C_i$  ( $i = 1 - 10$ ) and  $A_j$  ( $j = 1 - 5$ ) are given in ref 16 as functions of  $\lambda d$  ( $A_1 = 1.843$ ). Since the Yamakawa–Fujii theory considers no effect from the chain ends, it may not be used for short cylinders with  $L/d$  less than 4. Norisuye *et al.*<sup>17</sup> calculated the translational friction coefficient for wormlike cylinders capped with hemispheres at both ends. Their expression for  $R_H^{-1}$  near the rod limit, *i.e.*, for small  $\lambda L$ , reads

$$\begin{aligned}
 R_H^{-1} &= \frac{2}{L} [C'_1 \ln \sigma + C'_2 + C'_3(\lambda L) + C'_4(\lambda L)^2 \\
 &\quad + C'_5(\lambda L)^3 + C'_6(\lambda L)^4 + C'_7(\lambda L)^5] \quad (4)
 \end{aligned}$$

The coefficients  $C'_i$  are given in ref 17 as functions of  $\lambda d$  and  $\sigma$ . In the limit of  $L = d$ ,  $R_H$  given by eq 4

approaches  $d/2$  as expected by the Stokes law for spheres. The theoretical curves from eqs 3 and 4 are almost smoothly connected around  $L/d = 4$ .

The above expressions for  $R_H$  contain three parameters,  $L$ ,  $\lambda^{-1}$ , and  $d$ . The first parameter may be related to  $M_w$  by  $L = M_w/M_L$  with  $M_L$  being the molecular weight per unit contour length of the main chain. For low molecular weight polycromonomers, however, the effect from side chains near the main chain ends on  $L$  is not negligible<sup>10–12</sup> and may be taken into consideration by

$$L = M_w/M_L + \delta \quad (5)$$

where  $\delta$  stands for the hydrodynamic contribution of side chains to the main-chain contour (see Figure 3 of ref 10).

We computed  $R_H$  for F33 and F65 as functions of  $N_w$  from eqs 3–5 with the parameter sets<sup>10,12</sup> of  $\lambda^{-1}$ ,  $M_L$ ,  $d$ , and  $\delta$  explaining the  $M_w$ -dependence of  $[\eta]$ , with the result that the calculated  $R_H$  values for both polymers are appreciably smaller than the experimental ones. This was also the case for F15 in cyclohexane.<sup>11</sup> When  $d$  was varied with the other three parameters kept unchanged, the theoretical values came close to the data points over the substantial  $N_w$  ranges for the F33 and F65 polycromonomers. They are represented by the solid curves in Figure 4 and the parameters used for the calculation are summarized in Table II. We note that the intramolecular excluded-volume effect in toluene solutions of the F65 polymer should be negligible because  $\lambda L$  ( $= 4.5$ ) for the highest molecular weight sample is comparable to the critical Kuhn segment number (4–5) representing the onset of the volume effect in the other polycromonomers.<sup>9</sup>

For reference, our previous comparison between theory and experiment made for F15 in cyclohexane<sup>11</sup> is included in Figure 4, in which the solid line fitting the circles refers to the previously chosen parameters<sup>11</sup> ( $\lambda^{-1} = 11.5$  nm,  $M_L = 5600$  nm<sup>-1</sup>,  $d = 5.2$  nm, and  $\delta = 2.5$  nm). The dashed lines in the figure represent the theoretical values from eq 4 for  $\delta = 0$ . Their apparent deviation from the data points demonstrates that the effects from the chain ends are significant

**Table II.** Model parameters allowing fits to  $R_H$  data for polystyrene polycromonomers F33 and F65 in cyclohexane at 34.5 °C and F65 in toluene at 15 °C

Sample and Solvent	$\lambda^{-1}/\text{nm}$	$M_L/10^3 \text{ nm}^{-1}$	$d/\text{nm}$	$\delta/\text{nm}$
F33 in cyclohexane	22 (28) <sup>a</sup>	13,500	10 (7.4) <sup>b</sup>	4
F65 in cyclohexane	36	26,000	15 (11.5) <sup>b</sup>	6
F65 in toluene	75	25,000	18 (14) <sup>b</sup>	6

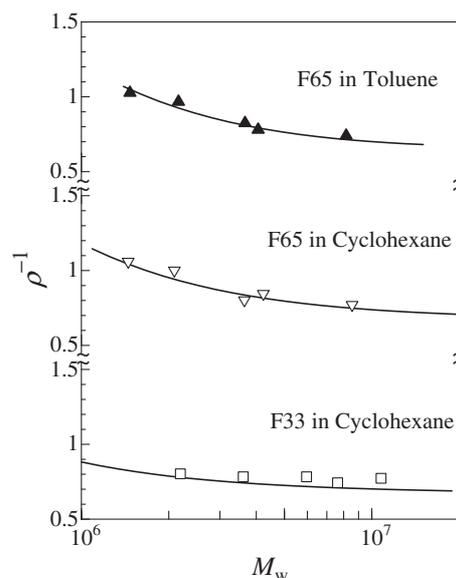
<sup>a</sup>value leading to a closer fit to  $R_H$  data (see the text) <sup>b</sup>values used to fit  $[\eta]$  data<sup>10,12</sup>

for  $N_w$  smaller than 100–200. We should point out, however, that these effects on  $R_H$  are not as remarkable as those observed on  $[\eta]$ .<sup>10,12</sup>

In Table II, the  $d$  values from  $R_H$  are about 1.29–1.35 times larger than those (in the parentheses) from  $[\eta]$ . This trend is similar to what was reported for thin stiff polymers;<sup>15</sup> in the typical case of poly(hexyl isocyanate) (PHIC) in hexane,<sup>18</sup> the  $d$  value estimated from the sedimentation coefficient (equivalent to  $R_H$ ) is about 1.5 times larger than that from  $[\eta]$ . This discrepancy in  $d$  is considered to come from certain shortcomings in the current hydrodynamic theories.<sup>13,16,19,20</sup> The polymacromonomers F33 and F65 (in either cyclohexane or toluene) are as stiff as the PHIC chain ( $\lambda^{-1} = 42$ –84 nm depending on the kind of solvent),<sup>15</sup> but their reduced diameters  $\lambda d$  (0.2–0.45) are one order of magnitude larger than that (0.02) for PHIC and comparable to those for typical linear flexible polymers.<sup>13</sup> In this sense, the polymacromonomers are hydrodynamically similar to flexible chains. This is indeed the case for the exponents of  $R_H$  already mentioned (see Figure 4).

According to detailed data analyses for linear polymer chains,<sup>13,15</sup> the hydrodynamic theories<sup>13</sup> are generally less accurate for a more flexible chain, *i.e.*, for a larger  $\lambda d$ , and the inaccuracy can lead to an appreciable error in the estimation of  $\lambda$  or  $M_L$ ; in the coil limit of the (unperturbed) wormlike chain,  $R_H$ ,  $[\eta]$ , and  $\langle S^2 \rangle$  are all determined by the product  $\lambda M_L$  [for example,  $R_H = (1/2A_1)(M/\lambda M_L)^{1/2}$  with  $M$  the molecular weight (see eq 3)]. For the F15 polymacromonomer in cyclohexane,<sup>11</sup> the value of  $(\lambda M_L)^{1/2}$  from  $R_H$  was 16% smaller than that from  $\langle S^2 \rangle$  or  $[\eta]$ , the discrepancy being more serious than that in  $d$ . We note that, although the  $[\eta]$  theory of Yoshizaki *et al.*,<sup>21</sup> used for our previous analyses,<sup>10,12</sup> is not accurate either in the coil limit, it gives  $(\lambda M_L)^{1/2}$  values consistent with those from  $\langle S^2 \rangle$  for the three polystyrene polymacromonomers in both cyclohexane and toluene, as was case for typical stiff chains.<sup>13,15</sup>

In the present analysis for F33 and F65, we allowed only  $d$  to change with the other parameters (from  $\langle S^2 \rangle$  or  $[\eta]$ ) kept unchanged, but in actuality, we can vary two of the four parameters in fitting  $R_H$  data for a given polymacromonomer.<sup>11</sup> If  $M_L$  and  $\delta$  are fixed to the values in Table II, a closer fit is obtained with  $\lambda^{-1} = 28$  nm and  $d = 10$  nm for F33 and thus the resulting  $(\lambda M_L)^{1/2}$  value is 11–13% smaller than that expected from  $\langle S^2 \rangle$  or  $[\eta]$  for the F33 polymer (we note that  $M_L = 1.3 \times 10^4$  nm<sup>-1</sup> from  $\langle S^2 \rangle$ ).<sup>9</sup> This finding bears a close resemblance to the discrepancy for the F15 polymer mentioned above. On the other hand, we found that neither  $\lambda^{-1}$  nor  $d$  needs to be altered for F65 (in the two solvents). Further discussion is given in relation to  $\langle S^2 \rangle$  in the next subsection.



**Figure 5.** Molecular weight dependence of reduced hydrodynamic radius  $\rho^{-1}$  ( $= R_H/\langle S^2 \rangle^{1/2}$ ) for polymacromonomers F33 and F65. Curves: theoretical values from eqs 3 and 6 with the parameters given in Table II.

#### Reduced Hydrodynamic Radius

Reduced hydrodynamic radii  $\rho^{-1}$  ( $= R_H/\langle S^2 \rangle^{1/2}$ ) for F33 in cyclohexane and F65 in cyclohexane and toluene are presented in the sixth column of Table I and plotted against  $\log M_w$  in Figure 5. It can be seen that  $\rho^{-1}$  for each polymacromonomer-solvent system decreases with increasing  $M_w$ , as was observed for linear flexible polymers with relatively low molecular weights in theta solvents,<sup>13</sup> and that this  $M_w$ -dependence is weaker for F33, *i.e.*, for the shorter side chain;  $\rho^{-1}$  for F15 in cyclohexane was almost independent of  $M_w$  over a range from  $6 \times 10^5$  to  $6.5 \times 10^6$ .<sup>11,14</sup> We note that the observed decreases in  $\rho^{-1}$  with increasing molecular weight are opposite to the behavior of PHIC<sup>18</sup> of high molecular weight.

The curves in Figure 5 represent the  $\rho^{-1}$  values calculated from eq 3 and the Benoit–Doty equation<sup>22</sup>

$$\langle S^2 \rangle = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} - \frac{1}{8\lambda^4 L^2} [1 - \exp(-2\lambda L)] \quad (6)$$

for  $\langle S^2 \rangle$  of an unperturbed wormlike chain using the model parameters in Table II; note that the contribution from side chains to  $\langle S^2 \rangle$  is insignificant for the polymacromonomers in the molecular weight range of interest. As may be expected from the discussion on the model parameters in the preceding subsection, the satisfactory agreement is seen for F65 in both cyclohexane and toluene. This substantiates that the available theories<sup>16,17,19,21</sup> for the wormlike chain are capable of consistently describing the  $M_w$ -dependence

of  $R_H$ ,  $[\eta]$ , and  $\langle S^2 \rangle$  for the F65 polymacromonomer. The wormlike chain with  $\lambda^{-1} = 84$  nm,  $M_L = 11,600$  nm $^{-1}$ ,  $d = 8$  nm, and  $\delta = 8$  nm also explains the  $M_w$ -dependence of  $D$  and  $\langle S^2 \rangle$  for the PMMA-PS polymacromonomer with  $M_0 = 2,900$  in toluene.<sup>1,2</sup> Interestingly, the backbone stiffness of this polymacromonomer is comparable to that of F65 in the same solvent, though, as mentioned in the Introduction,  $[\eta]$  data for the former polymer are inconsistent with  $\langle S^2 \rangle$  and thus remain to be seen by experiment.

The calculated curve for F33 in Figure 5 deviates slightly downward from the data points, reflecting the fact that the parenthesized  $\lambda^{-1}$  value of 28 nm (instead of 22 nm) in Table II leads to a closer fit to the  $R_H$  data in Figure 4. This difference in  $\lambda^{1/2}$  or  $(\lambda M_L)^{1/2}$  is about the same as that [16% in  $(\lambda M_L)^{1/2}$ ] found previously for the F15 polymacromonomer, both coinciding with the error of theoretical  $D$  in the coil limit<sup>13,15</sup> due to the ignored effect of fluctuating hydrodynamic interaction. As was shown by Yamakawa and Yoshizaki,<sup>23</sup> this effect is negligible in the stiff chain limit, so that consistent values for  $\lambda$  and  $M_L$  may be obtained from  $\langle S^2 \rangle$  and  $D$  data for thin stiff chains. The point is that this is not always the case for polymacromonomers which have stiff backbones but large reduced diameters  $\lambda d$  as in linear flexible polymers.

In view of the theoretical problem revealed in the present work, the inconsistent  $d$  values from  $R_H$  and  $[\eta]$  are probably beyond our discussion. Very recently,<sup>14</sup> we determined the diameter of the F15 polymacromonomer molecule in cyclohexane by small-angle X-ray scattering. The average value obtained for most samples was 4.8 nm, being close to both 5.2 nm (from  $D$ )<sup>11</sup> and 4.7 nm (from  $[\eta]$ ).<sup>10</sup>

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## REFERENCES

1. M. Wintermantel, M. Schmidt, Y. Tsukahara, K. Kajiwara, and S. Kohjiya, *Macromol. Rapid Commun.*, **15**, 279 (1994).
2. N. Nemoto, M. Nagai, A. Koike, and S. Okada, *Macromolecules*, **28**, 3854 (1995).
3. M. Wintermantel, M. Gerle, K. Fischer, M. Schmidt, I. Wataoka, H. Urakawa, K. Kajiwara, and Y. Tsukahara, *Macromolecules*, **29**, 978 (1996).
4. S. Kawaguchi, K. Akaike, Z.-M. Zhang, H. Matsumoto, and K. Ito, *Polym. J.*, **30**, 1004 (1998).
5. K. Fischer and M. Schmidt, *Macromol. Rapid Commun.*, **22**, 787 (2001).
6. S. Desvergne, V. Héroguez, Y. Gnanou, and R. Borsali, *Macromolecules*, **38**, 2400 (2005).
7. O. Kratky and G. Porod, *Recl. Trav. Chim. Pays-Bas*, **68**, 1106 (1949).
8. K. Terao, Y. Takeo, M. Tazaki, Y. Nakamura, and T. Norisuye, *Polym. J.*, **31**, 193 (1999).
9. K. Terao, Y. Nakamura, and T. Norisuye, *Macromolecules*, **32**, 711 (1999).
10. K. Terao, T. Hokaajo, Y. Nakamura, and T. Norisuye, *Macromolecules*, **32**, 3690 (1999).
11. K. Terao, S. Hayashi, Y. Nakamura, and T. Norisuye, *Polym. Bull.*, **44**, 309 (2000).
12. T. Hokaajo, K. Terao, Y. Nakamura, and T. Norisuye, *Polym. J.*, **33**, 481 (2001).
13. H. Yamakawa, "Helical Wormlike Chains in Polymer Solutions," Springer-Verlag, Berlin, 1997.
14. K. Amitani, K. Terao, Y. Nakamura, and T. Norisuye, *Polym. J.*, **37**, 324 (2005).
15. T. Norisuye, *Prog. Polym. Sci.*, **18**, 543 (1993).
16. H. Yamakawa and M. Fujii, *Macromolecules*, **6**, 407 (1973).
17. T. Norisuye, M. Motowoka, and H. Fujita, *Macromolecules*, **12**, 320 (1979).
18. H. Murakami, T. Norisuye, and H. Fujita, *Macromolecules*, **13**, 345 (1980).
19. H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 128 (1974).
20. H. Yamakawa and T. Yoshizaki, *Macromolecules*, **13**, 633 (1980).
21. T. Yoshizaki, I. Nitta, and H. Yamakawa, *Macromolecules*, **21**, 165 (1988).
22. H. Benoit and P. Doty, *J. Phys. Chem.*, **57**, 958 (1953).
23. H. Yamakawa and T. Yoshizaki, *J. Chem. Phys.*, **91**, 7900 (1989).