Dimensional and Hydrodynamic Factors for Flexible Star Polymers in the Good Solvent Limit

Kazuhito Shida,[†] Kaoru Ohno,*[,†] Masayuki Kimura,[‡] Yoshiyuki Kawazoe,[†] and Yo Nakamura[§]

Institute for Materials Research, Tohoku University, Sendai 980-77, Japan, Japan Advanced Institute of Science and Technology, Asahidai, Tatsunokuchi-machi, Nomi-gun, Ishikawa 901-21, Japan, and Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, Japan

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ABSTRACT: Star chains composed of arms with uniform length were generated on a simple cubic lattice by the Monte Carlo method using the enrichment algorithm, which enabled us to obtain chains with total segment numbers (N) up to 1200. The number of arms (f) ranged from 2 to 24. The radius of gyration ($\langle S^2\rangle^{1/2}$), the dimensionless intrinsic viscosity (E), and the hydrodynamic radius (R_H) were evaluated as functions of f and N by averaging over more than 4000 samples. The calculations of E and R_H were made according to Zimm's method. It was found that the radius expansion factor (α_S) for star chains with long arms obeys the relation $\alpha_S^2 = 1.53z^{2/5}$, which is known for long flexible linear chains, where z is the excluded volume parameter. The ratios of $\langle S^2\rangle$, E, and R_H of star chains to those for linear chains were evaluated as functions of f. These ratios obtained and the Flory factors for the intrinsic viscosity and R_H extrapolated to $N^{-1/2} \rightarrow 0$ reproduced experimental data well.

Introduction

Measurable quantities such as the mean-square radius of gyration ($\langle S^2\rangle$), the intrinsic viscosity ($[\eta]$), and the hydrodynamic radius (R_H) are some of the central and important properties in dilute solutions of linear polymers or other polymers with various architectures such as stars which have attracted current interests. Those quantities for star polymers are characterized by the star-to-linear ratios g_S, g_η, and g_H[1,2] (for $\langle S^2\rangle$, $[\eta]$, and R_H, respectively), where each ratio is evaluated at the same molecular weight. Theoretical prediction of these ratios in the good solvent limit is very difficult because the two effects, excluded volume and hydrodynamic interactions between segments of the chain, should be considered. The former effect may be treated by the renormalization group theory,[3] although the ϵ-expansion method sometimes makes erroneous results because of its poor convergency.[4] Theoretical equations of the hydrodynamic parameters g_H and g_η for Gaussian polymers without excluded volume effect were derived by Stockmayer and Fixman[5] and Zimm and Kilb,[6] respectively. However, they failed to explain the experimental data quantitatively probably because of errors arising from the preaveraging approximation of the Oseen tensor.

Zimm[7−9] applied the Monte Carlo method to the Kirkwood−Riseman equation[10] to evaluate hydrodynamic quantities without invoking the preaveraging approximation. Wilkinson et al.[11] calculated the ratios for star chains on a lattice by Zimm's method. However, their simulation data are confined to total segment numbers (N) of less than 60 and arm numbers (f) of 1, 3, and 6. The simulation data by Freire et al.[12,13] in the 1980s are also insufficient for the same reason. To obtain accurate values of the ratios in the limit of $N \rightarrow \infty$, the simulation should be extended to larger N and various f values.

Recently, Ohno and Binder[14] proposed the enrichment algorithm for generating lattice polymers which is free from the biased sampling and suitable for generating huge star molecules. A recent investigation on the second virial coefficients for star polymers[4] showed that this algorithm is suitable for studying dilute solution properties of polymers. In this work, uniform star polymers on a simple cubic lattice were generated by this method to evaluate the star-to-linear ratios for $\langle S^2\rangle$, $[\eta]$, and R_H. Here, *uniform* means that each star chain is made of arms with the same length. The maximum segment numbers studied are 1-order of magnitude larger than those of Wilkinson et al.[11]

We use Zimm's method[7] to evaluate the hydrodynamic properties because of the simpleness of the algorithm. This method includes the rigid-body approximation, which is known not to give exact results.[15] However, errors arising from it do not seem serious. This is discussed through the comparison of our data with those obtained recently by Freire et al.[16] up to $N = 325$ without that approximation.

Methodology

Enrichment Algorithm. Monte Carlo simulations of hydrodynamic properties are carried out in a 2-fold approach. In the first part, a statistical ensemble of chains is generated. In the second part, hydrodynamic properties are calculated on an appropriate hydrodynamic model for each configuration and the ensemble average is taken.

Adoption of trajectories on the lattice as polymer chains is advantageous to Monte Carlo simulation because of the simplicity of the calculation process. However, the chains on the lattice are different from real polymers when the number of segments is small, and much longer chains are desirable to make lattice chains closer to actual polymer chains, although very long self-avoiding chains on the lattice are not easy to generate. Generally, increasing both the number of chains and the length of the chains causes reduction of the efficiency of sampling algorithm and protracts the necessary CPU time in computation. Moreover, today's supercomputers are not ideally suitable for these kinds of nonnumerical algorithms. For this reason, an efficient sampling technique is required to

[†] Tohoku University.
[‡] Japan Advanced Institute of Science and Technology.
[§] Osaka University.

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perform the simulation for large-scale systems. For the generation of such an ensemble, the enrichment algorithm proposed by Ohno and Binder[14] is efficient and employed in this work. This algorithm is based on the stepwise elongation of each chain and is suitable for producing efficiently an ensemble of multichain polymer systems including star polymers.

On a simple cubic lattice, star chains with f arms are modeled as f self-avoiding subchains whose ends are in contact with each other. In actuality, the production of the sample configurations of stars begins at a polyhedral core with the first f segments set on it. This core represents the center unit of the star polymer. For relatively small f, a simple octahedron was used as the center unit. For f greater than 6, larger center units[14] are used. But the effects from the size and shape of the center units should be negligible for stars with sufficiently long arms.

At the first stage of the simulation, there are a large number (m_1) of samples, each having one segment in every arm starting from the same center unit. They are the first ($l = 1$) *generation* of samples. In the lth iteration, one segment is added to every arm end of the sample, which is chosen from m_l samples of the lth generation, according to a pseudorandom number. The direction of elongation is treated with the same probability. For each generation, s attempts of producing new samples are made. The resulting configurations are candidates for the $(l + 1)$th generation of samples. All of these sm_l candidates must be checked in terms of the self-avoiding constraint. All samples which do not fulfill the constraint are eliminated.

Now we have obtained psm_l candidates, where p is the success rate in the geometrical checking of samples. We can choose m_{l+1} samples randomly from these candidates and regard them as the $(l + 1)$th generation of samples. This procedure is repeated until each arm has the desired length L ($=N/f$), and through this process, with an appropriate value of s, we obtain the desired number of samples of the f-arm star-shaped polymer. The number of samples, m_l, should be increased as l increases, to keep the simulation from an unphysical bias. Since p is not a changeable parameter, we must choose s carefully so as to satisfy $ps \gg 1$.

Hydrodynamic Interaction. In the calculation of hydrodynamic properties, use is often made of the rigid-body approximation, in which the polymer chains in the flow are assumed to move as if they are rigid molecules;[17] i.e., their equilibrium conformations are preserved in the flow. This approximation leads to the Kirkwood−Riseman equation[10] for a single polymer molecules; i.e.,

$$\frac{1}{6\pi\eta_0 a}\boldsymbol{F}_i + \sum_{i\neq j}\boldsymbol{T}_{ij}\boldsymbol{F}_j - \boldsymbol{u}_i = -v_i^0 \tag{1}$$

Here, η_0 is the viscosity of the fluid, a the hydrodynamic radius of each segment of the chain, $\boldsymbol{F}_i = (F_{ix}, F_{iy}, F_{iz})$ the frictional force exerted on the ith segment, and $\boldsymbol{T}_{ij}$ the Oseen tensor[18] defined by

$$\boldsymbol{T}_{ij} = \frac{1}{8\pi\eta_0 r_{ij}}\left\{\boldsymbol{I} + \frac{\boldsymbol{r}_{ij}\boldsymbol{r}_{ij}}{r_{ij}^2}\right\} \tag{2}$$

Here, $\boldsymbol{r}_{ij}$ is the distance between the ith and jth segments. Taking the center of mass as the origin, the velocity $\boldsymbol{u}_i = (u_{ix}, u_{iy}, u_{iz})$ of the ith segment at the position (x_i, y_i, z_i) is given by

$$u_{ix} = u_x - y_i\Omega_z \qquad u_{iy} = u_y - x_i\Omega_z \qquad u_{iz} = u_z \tag{3}$$

where (u_x, u_y, u_z) is the velocity of the center of mass of the chain and Ω_z the angular velocity about the z axis. The velocity $\boldsymbol{v}_i^0$ of the external flow at the position of the ith segment is taken to be

$$\boldsymbol{v}_i = (\kappa z_i/2, 0, \kappa x_i/2) \tag{4}$$

with the shear rate (κ) set equal to 2.

If the positions of the segments of a Monte Carlo chain are given, eq 1 with eqs 2−4 can be solved under the following additional conditions:

$$\Omega_z = 0 \tag{5}$$

and

$$\sum_i \boldsymbol{F}_i = N\boldsymbol{e}_z \quad [=(0, 0, F_z)] \tag{6}$$

for the calculation of R_H and

$$\sum_i (y_i F_{ix} - x_i F_{iy}) = 0 \tag{7}$$

and

$$\sum_i \boldsymbol{F}_i = 0 \tag{8}$$

for the calculation of the intrinsic viscosity.

Once the equation is solved, R_H is given by

$$R_H = F_z/6\pi\eta_0 u_z \tag{9}$$

and the dimensionless intrinsic viscosity (E) by

$$E = 2\sum_i (z_i F_{ix})/N\kappa\eta_0 b^3 \tag{10}$$

which is related to $[\eta]$ by

$$E = 2M[\eta]/N_A N b^3 \tag{11}$$

Here, M is the molecular weight, N_A the Avogadro constant, and b the bond length (=1).

To make calculations as close as possible to the asymptotic region, the length of the arms (L) should be especially large. In the present study, the typical values of s and the maximum L are 20 and 200, respectively, m_L is from 4300 to 15 000, and f ranges from 2 to 24. The controllable parameter a was taken to be one-fourth of the bond length and half of the bond length. The latter represents the beads touching neighboring ones and seems more realistic. However, it is known[11,19] that the hydrodynamic quantities calculated using the former model reach more rapidly to the asymptotic behavior in the non-free-draining limit which is commonly observed in polymer solutions.

All calculations have been carried out on a Hitachi S-3800 computer.

Results and Discussion

Radius of Gyration. Figure 1 shows double-logarithmic plots of $\langle S^2\rangle^{1/2}/f$ against N for different f's. Except for $f = 24$, the plotted points for any f can be fitted by a straight line of the form

$$\langle S^2\rangle^{1/2} = A(f)N^{0.6} \tag{12}$$

provided that L ($=N/f$) $\gtrsim 10$. The values of $A(f)$ are presented in the second column of Table 1, and the values of g_S calculated from $A(f)/A(2)$ are shown in the third column. These values are close to those obtained by Whittington et al.[20] ($f = 3, 4, 5, 6$) and Rubio and Freire[21] ($f = 4, 6, 12, 18$). The table also includes g_S values calculated by the Zimm−Stockmayer equation[22]

$$g_S = (3f - 2)/f^2 \tag{13}$$

for Gaussian chains. The simulation data are very close to the values from this equation, confirming Barrett and

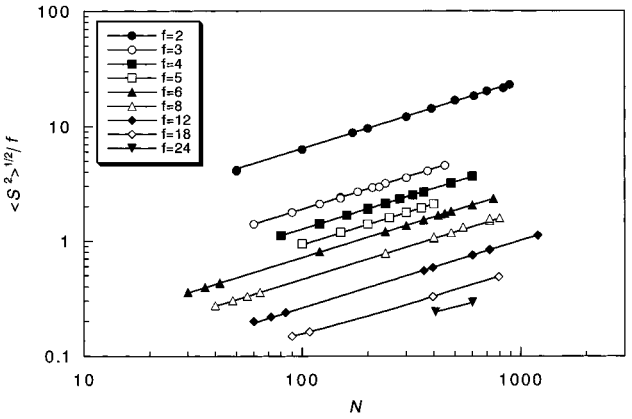

Figure 1. Radii of gyration $\langle S^2\rangle^{1/2}$ of star chains (divided by the arm number f) plotted against the total segment number N.

Table 1. Dimensional Factors for the Radius of Gyration of Monte Carlo Star Chains

f	$A(f)$	g_S	g_S (Gauss)
2	0.43		
3	0.38	0.78	0.778
4	0.34	0.63	0.625
5	0.31	0.52	0.520
6	0.29	0.45	0.444
8	0.25	0.34	0.344
12	0.21	0.24	0.236
18		(0.16)[a]	0.160

[a] Estimated from two data for $N > 300$.

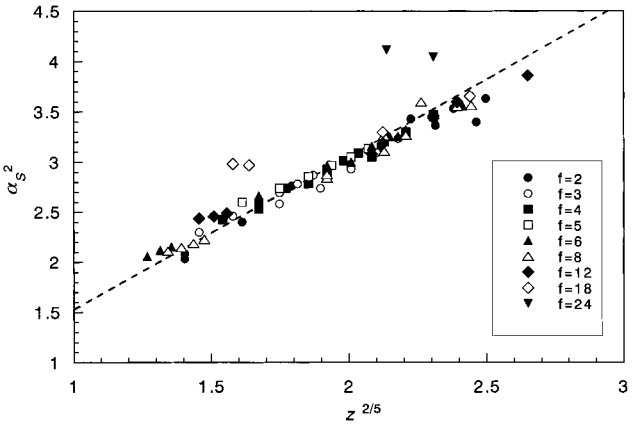

Figure 2. Square-radius expansion factor α_S^2 for star chains with f arms plotted against $z^{2/5}$.

Tremain's[23] simulation on self-avoiding star chains. This finding is consistent with the experimental fact that g_S is insensitive to solvent quality.[2] The renormalization group theory of Douglas and Freed[24] also predicts that the difference between g_S values in the unperturbed state and in the good solvent limit does not exceed more than a few percent.

The radius expansion factor (α_S) defined by $\langle S^2\rangle^{1/2}/\langle S^2\rangle_0^{1/2}$ can be calculated if $\langle S^2\rangle_0$ ($\langle S^2\rangle$ in the unperturbed state) is evaluated from $\langle S^2\rangle_0 = (Nb^2/6)g_S$ with eq 13. Here, b is the bond length and equal to 1 for our model. Figure 2 shows the plots of α_S^2 against $z^{2/5}$, where z is the excluded volume parameter defined by[25]

$$z = (3/2\pi b^2)^{3/2}\beta N^{1/2} \tag{14}$$

Here, β is the binary-cluster integral and was taken to be the volume occupied by one lattice cell (=1).[26] The

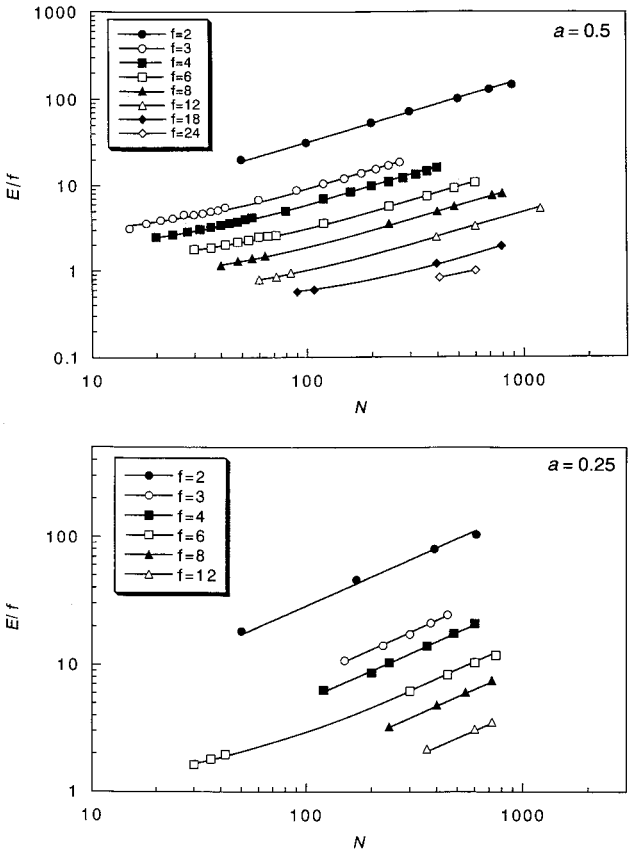

Figure 3. Dimensionless intrinsic viscosities E (divided by the arm number f) of star chains plotted against the total segment number N: upper, $a = 0.5$; lower, $a = 0.25$; a is the hydrodynamic radius of each segment.

data points for different f's are seen to merge at high z, showing that linear and star chains are swollen in good solvents by the same ratio if the molecular weights are the same. This is equivalent to the fact that g_S is essentially independent of solvent quality.

The dashed line in Figure 2 represents the relation $\alpha_S^2 = 1.53z^{2/5}$ known for linear lattice chains of $N \gtrsim 20$.[27] It closely fits our simulation data for f smaller than 8 in the region $\alpha_S^2 \gtrsim 2$. This behavior of α_S^2 for star chains cannot be explained by smoothed density theories,[28] which predict α_S to become larger with increasing segment density in the chain if the number of segments is kept constant. The blob theory of Daoud and Cotton[29] also fails to explain the f-independent behavior of α_S, because it predicts $\alpha_S^2 \propto f^{1/5}$.

The reliability of the Daoud−Cotton theory has been discussed in terms of the dependence of g_S on f. However, the difference between g_S values predicted by this theory and eq 13 cannot be detected from the usual simulations for $f < 10$.[23,30] The radius expansion factor is more sensitive: for example, α_S^2 for $f = 10$ is 1.6 times as large as that for $f = 1$ if the Daoud−Cotton theory is correct. But we cannot recognize such a behavior in Figure 2 and conclude that it is not an accurate theory. Note that here we focus on the behavior of the radius of star polymers with infinitely long arms. Stars with many short arms may be treated by the theory.

The convergency of the data points to the dashed line in Figure 2 becomes slower as f increases. The data for $f = 12$ obey this line at $\alpha_S^2 \gtrsim 2$ and those for $f = 18$ at $\alpha_S^2 \gtrsim 3$. The data for $f = 24$ do not reach the line even at $N = 600$. This may be due to the crowdedness of

Table 2. Factors for the Intrinsic Viscosity of Monte Carlo Star Chains

	$a = 0.5$		$a = 0.25$	
f	$B(f)$	g_η	$B(f)$	g_η
2	1.10		0.92	
3	0.95	0.86	0.75	0.82
4	0.80	0.73	0.68	0.74
6	0.61	0.55	0.52	0.57
8	0.49	0.45	0.42	0.46
12	0.37	0.34	0.30	0.33
18		(0.25)[a]		

[a] Estimated from two data for $N > 300$.

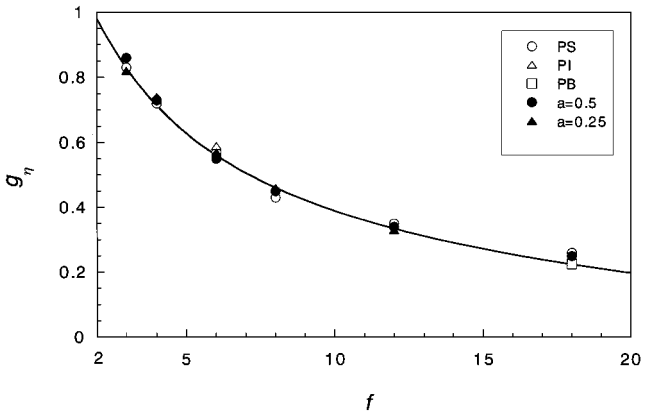

Figure 4. Plots of g_η vs f for star chains on the lattice (filled symbols). Unfilled symbols, experimental data;[2] solid line, values calculated from eq 16.

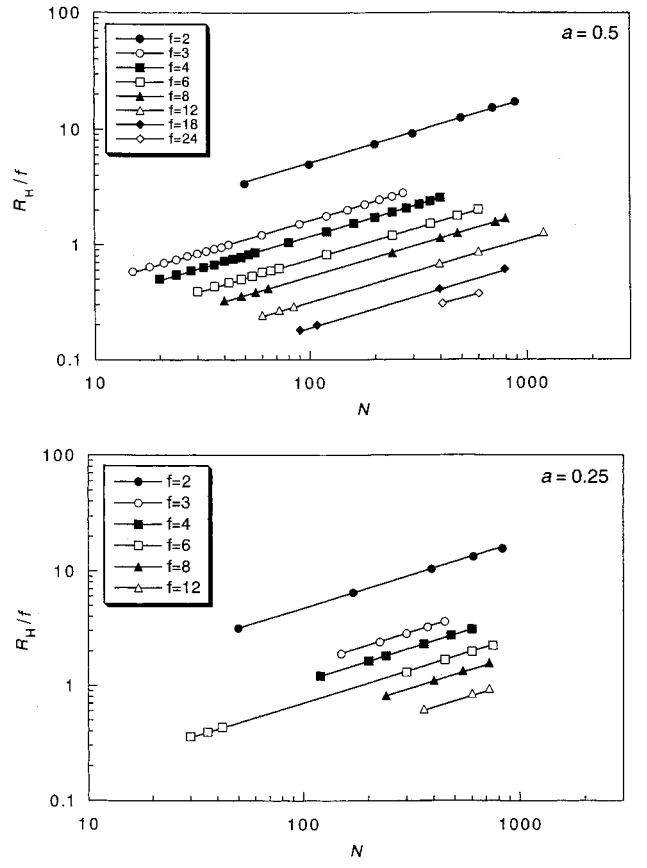

Figure 5. Hydrodynamic radii R_H (divided by the arm number f) of star chains plotted against N: upper, $a = 0.5$; lower, $a = 0.25$.

segments near the molecular center, where each arm is more extended than near its extremity.

Table 3. Factors for the Hydrodynamic Radius of Monte Carlo Star Chains

	$a = 0.5$		$a = 0.25$	
f	$C(f)$	g_H	$C(f)$	g_H
2	0.41		0.33	
3	0.38_7	0.94	0.31_5	0.95
4	0.37_6	0.92	0.30_4	0.92
6	0.35_4	0.86	0.29_4	0.89
8	0.33_6	0.82	0.27_2	0.82
12	0.30	0.73	0.24	0.73
18	0.27	0.66		

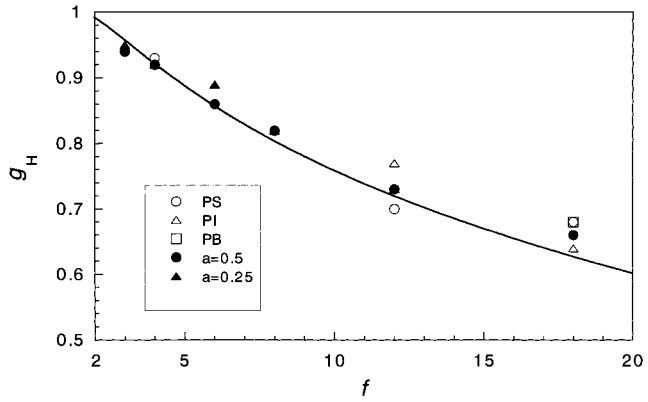

Figure 6. Plots of g_H vs f for star chains on the lattice (filled symbols). Unfilled symbols, experimental data;[2] solid line, values calculated from eq 18.

Intrinsic Viscosity. The dimensionless intrinsic viscosity values calculated for the hydrodynamic bead radius, $a = 0.5$ and $a = 0.25$, are double-logarithmically plotted against N in Figure 3; they are again divided by f. The data for every arm number (except $f = 24$) can be represented by

$$E = B(f)N^{\nu} \tag{15}$$

for $L \gtrsim 10$. The values of the exponent ν for $a = 0.5$ and $a = 0.25$ are 0.73 and 0.75, respectively. They are close to the experimentally observed values (around 0.75) for flexible chains in good solvents. The values of $B(f)$ are summarized in Table 2 along with g_η evaluated from $B(f)/B(2)$. It can be seen that the g_η values for the two a's are close to each other. Our values are not so different from those obtained by Wilkinson et al.[11] ($f = 3, 4, 6$) and Rey et al.[13] ($f = 6, 12, 18$), although N of these data is confined to less than 60. The dependence of g_η on f is shown in Figure 4, in which experimental data for polystyrene (PS), polyisobutyrene (PIB), and polybutadiene (PB) in good solvents[2] are also included. The agreement between the simulation and experimental values are quite good.

The solid line in Figure 4 represents the values calculated from the equation of Douglas et al.[2]

$$g_\eta = \left(\frac{3f-2}{f^2}\right)^{0.58} \frac{0.724 - 0.015(f-1)}{0.724} \tag{16}$$

It fits the simulation data very well. We note that eq 16 was derived semiempirically to fit the experimental data.

Hydrodynamic Radius. Figure 5 shows the N dependence of R_H/f for $a = 0.5$ and $a = 0.25$. The data points for each f can be fitted by a straight line of the form

$$R_H = C(f)N^{\mu} \tag{17}$$

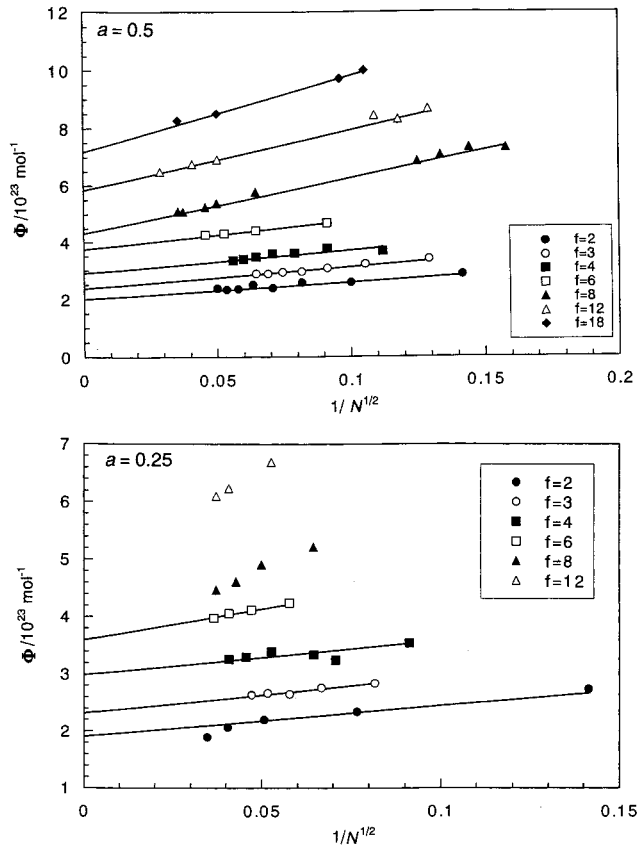

Figure 7. Flory viscosity factor Φ for stars plotted against $N^{-1/2}$: upper, $a = 0.5$; lower, $a = 0.25$.

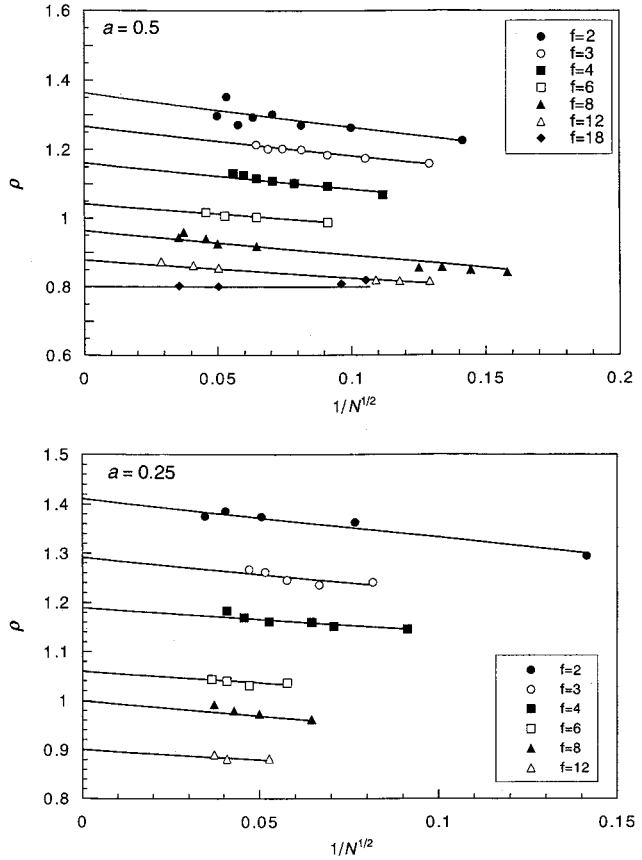

Figure 8. Hydrodynamic factor ρ for stars plotted against $N^{-1/2}$: upper, $a = 0.5$; lower, $a = 0.25$.

for $L \gtrsim 10$. The exponents μ for $a = 0.5$ and 0.25 are 0.55 and 0.58, respectively. The values of $C(f)$ obtained

Table 4. Flory Factors for the Intrinsic Viscosity and Hydrodynamic Radius Extrapolated to Infinite *N*

	$10^{-23}\Phi$ mol^{-1}		ρ	
f	$a = 0.5$	$a = 0.25$	$a = 0.5$	$a = 0.25$
2	2.0	1.9	1.36	1.41
3	2.3	2.3	1.26	1.29
4	2.9	3.0	1.16	1.19
6	3.7	3.6	1.04	1.06
8	4.3		0.97	1.00
12	5.8		0.88	0.9
18	7.2		0.80	

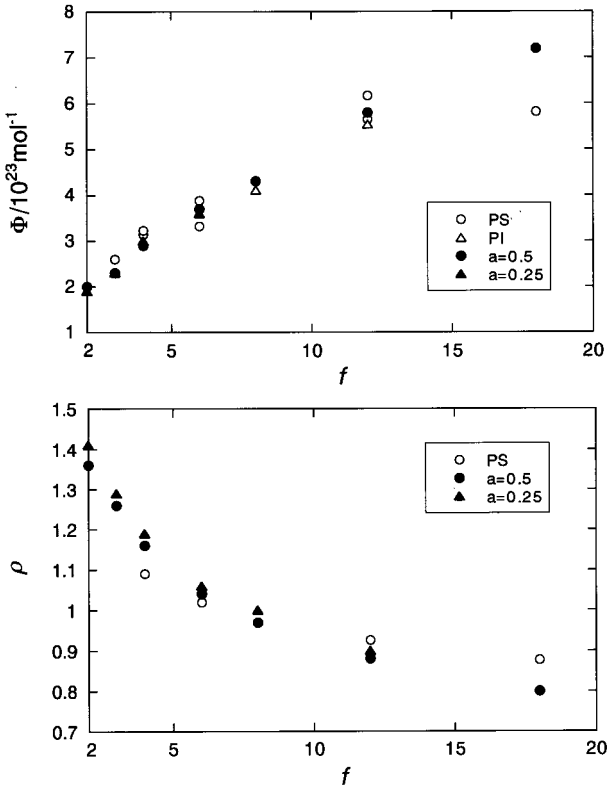

Figure 9. Comparison of the Flory factors (at infinite N) with experimental data for polystyrene[2,32–36] and polyisoprene.[37]

are summarized in Table 3 along with those of the g_H evaluated from $C(f)/C(2)$. There are no substantial differences between our data and those reported in the 1980s for $N < 60$.[11–13]

These g_H values are compared with the experimental data[2] in Figure 6. The agreement is satisfactory, as is the case for g_η. The solid line in the figure represents the semiempirical equation of Douglas et al.,[2] i.e.,

$$g_H = \frac{f^{1/4}}{[2 - f + \sqrt{2}(f-1)]^{1/2}} \frac{0.932 - 0.0075(f-1)}{0.932} \tag{18}$$

which slightly underestimates g_H only for very large f.

Flory Factors. The values of the Flory viscosity factor,[31] Φ [$\equiv[\eta]M/(6\langle S^2\rangle)^{3/2}$], and the hydrodynamic factor, ρ [$\equiv\langle S^2\rangle^{1/2}/R_H$], are plotted against $1/N^{1/2}$ in Figures 7 and 8, respectively. These factors seem to approach the rigid-sphere values ($\Phi = 9.23 \times 10^{23}$ mol^{-1} and $\rho = 0.775$) with increasing f. The values of Φ and ρ extrapolated to $1/N^{1/2} \to 0$ for $a = 0.5$ and $a = 0.25$ are summarized in Table 4. The values of $10^{-23}\Phi$ mol^{-1} for $f = 2$ and 12 are close to those (1.80 and 5.18 for $f = 2$ and $f = 12$, respectively) obtained by Freire et al.[16] from simulations without the rigid-body approxi-

mation. This shows that the approximation does not make as much of an error on viscosity values. In Figure 9, the values obtained from the simulation are compared with the experimental data for polystyrene[2,32−36] and polyisoprene.[37] The simulation data agree well with the experimental data, showing that our Monte Carlo simulation consistently and quantitatively explains the dimensional and hydrodynamic properties of star polymers in good solvents.

Conclusions

Monte Carlo simulations concerning the dimensional and hydrodynamic properties of star polymers have been conducted under the self-avoiding condition, which can be regarded as the good solvent limit. The size of the stars, which is crucial for obtaining the results in the asymptotic region, is far extended by means of an efficient sampling technique. It is found that the radius expansion factors for simulated star chains with long arms obey the asymptotic relation known for long linear chains. The simulation is also shown to provide nice reproductions of the experimental results both for the hydrodynamic radius and the intrinsic viscosity. The observed good agreements suggest that the rigid-body approximation is not bad. We are now planning to extend the present simulation to chains of various architectures in good and Θ solvent systems.

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