Arm-number dependence of dimensions of star-shaped polystyrene in a good solvent

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Radii of gyration R_g and hydrodynamic radii R_h of star-shaped polystyrenes with different arm numbers and their arm polymers were measured in toluene solution by static and dynamic light scattering. R_h depends on the number of arms f stronger than R_g. The ratios $g_g^a = R_g(\text{star})/R_g(\text{arm})$ and $g_h^a = R_h(\text{star})/R_h(\text{arm})$ were compared with other experimental and computer simulation results to examine the universality of these ratios. Universality of the relation of g_g^a *versus* number of arms f is confirmed. No clear indication of failure of g_h^a in universality is observed, and it was suggested that g_h^a is not sensitive to systems. Experimental results were also compared with available theories. The renormalized two-parameter theory by Douglas and Freed for static quantities g_g^a and g_A $(= A_2(\text{star})/A_2(\text{linear})$, where A_2 is the second virial coefficient) reproduces the experimental data very well at lower fs and agreement in g_g^a is excellent over a wide range of f.

(Keywords: star-shaped polystyrene; hydrodynamic radius; radius of gyration; universal ratio)

INTRODUCTION

A study of chain dimensions of a branched polymer in solution is quite an interesting theoretical subject and also has practical importance because it will afford a foundation to establish a method for characterizing branched polymers. Owing to their high structural regularity, star-shaped polymers have been the most extensively investigated. In the last decade, new theoretical techniques such as the blob concept[1] and the renormalization group calculation[2-6] have been applied to the study of static properties of star-shaped polymers. These theories give greater importance to the long-range correlation of local monomer concentration in a solution than the classical theory which relies on Gaussian chain statistics. Owing to the advance in synthetic techniques, many experimental investigations of star-shaped polymers have also been made in recent years. To know the universal behaviour of star-shaped polymers, it is necessary to study various different systems. Star-shaped polyisoprenes with a wide variety of numbers of arms have been extensively investigated by Bauer *et al.*[7] while other systems, for example star-shaped polystyrenes, have not been so extensively studied.

The theoretical calculation of hydrodynamic quantities is much more difficult than that of static quantities. The above-mentioned new theoretical techniques have not been applied to the calculation of hydrodynamic quantities of star-shaped polymers even in the limit of strong hydrodynamic interaction (non-free-draining), and only classical theory is available. Computer simulations of hydrodynamic behaviour of star-shaped polymers need a long computational time and are still limited to the study of small numbers of arms or short arm lengths. Compared with difficulty encountered in theoretical investigations or computer simulations, the experimental evaluation of hydrodynamic quantities is relatively simple. Though the hydrodynamic radius is more easily obtained than the radius of gyration, hydrodynamic radii of star-shaped polymers have not been so extensively measured as their radii of gyration. Therefore an understanding of the hydrodynamic behaviour of star-shaped polymers is still poor and accumulation of reliable experimental data is necessary.

In the present study, two series of star-shaped polymers with up to 22 arms were synthesized, and both static and dynamic light scattering measurements of these samples in a good solvent were carried out. The results were compared with other experimental studies, computer simulations and theories. The dependence of the radius of gyration and hydrodynamic radius on the number of arms were studied. Universality of the ratios of radii between a star-shaped polymer and its arm were examined.

EXPERIMENTAL

Samples

Two series (NF and LS) of star-shaped polystyrenes were prepared. Each series forms a group of polymers with arms with the same degree of polymerization.

A sample of the NF series was synthesized by coupling living arm polymers onto a low molecular weight polymer centre. Poly(4-vinylphenyldimethylvinylsilane) (PVS) was used as the centre and its monomer VS was synthesized from 4-chlorostyrene and vinyldimethylchlorosilane by the Grignard reaction in tetrahydrofuran (THF). The monomer was first dried over calcium hydride and then purified by repeated distillation in the

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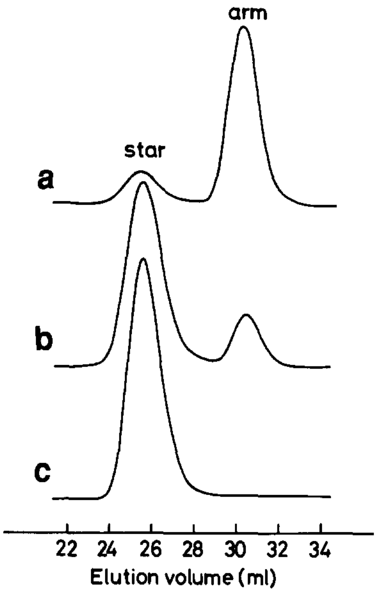

Figure 1 Gel permeation chromatograms of a sample (NF-1) in the purification process: (a) after coupling; (b) after crude fractionation by precipitation; (c) after g.p.c. fractionation

presence of sodium n-octylbenzophenone in a sealed vacuum[8]. PVS was polymerized in THF at −78°C with cumyl potassium as an initiator. Special care was taken to ensure that the reaction time did not exceed 5 min in order to suppress the side reaction of living anions attacking silylvinyl groups. Four different molecular weight centre polymers were prepared. PVSs were fractionated by using a preparative gel permeation chromatography (g.p.c.) apparatus (Tosoh Co. HLC-837) with two G2000H and one GMH columns.

The arm polymer, living polystyryl anion, was prepared in benzene with sec-butyllithium as an initiator and was end-capped with a few units of butadiene to reduce the influence of steric effects in the subsequent coupling reaction[9]. Four fractions of living arm polymer solution taken out of a single reaction vessel were mixed with respective benzene solutions of PVS samples prepared previously. An excess amount of living polymer was used to ensure the completion of coupling. After these mixtures were allowed to stand for ~1 week, residual living polymers were terminated by degassed n-butanol. After crude fractionation by a precipitation method using benzene and methanol as solvent and non-solvent, star-shaped polymers were further fractionated by using preparative g.p.c. apparatus with two G5000H and one GMH columns. Gel permeation chromatograms of a sample (NF-1) are shown in *Figure 1*. No arm polymer was detected in the final product.

The LS series was originally prepared for a study of the dimensions of a labelled part in a star-shaped polymer by small angle neutron scattering[10]. In the LS series, a triblock copolymer of deuterated (labelled) styrene, protonated styrene and protonated VS was synthesized first, then protonated living arm polystyrene was coupled to the VS block of this copolymer. The degree of polymerization of the living arm polystyrene, which was prepared by the same method as described above, was adjusted approximately to that of the styrene block in the triblock copolymer. The coupling reaction and fractionation of these star-shaped polymers were carried out in the same way as for the preparation of the NF series. Details of sample preparation of the LS series will be described elsewhere[10].

At each step of the sample preparation in both series, a small amount of sample was taken from the reaction vessel for subsequent characterization.

Toluene, used as the solvent, of reagent grade was dried over calcium hydride and purified by fractional distillation.

Characterization

Number-average molecular weights (M_n) of the centre polymers of the NF series were determined by measuring vapour pressures of benzene solutions at 40°C with Corona Electric 117. The M_ns of triblock copolymers of the LS series and arm polymers of both series were determined from osmotic pressures of toluene solutions at 30°C measured with a membrane osmometer Hewlett-Packard 502. The weight-average molecular weights (M_w) of arm polymers were determined by light scattering measurements described below. The composition of each block in the triblock copolymers (LS series) was determined from ^1H n.m.r. spectra obtained on a 270 MHz Jeol JNR-GX270 spectrometer, by the use of molecular weights of the first blocks obtained using analytical g.p.c. apparatus (Tosoh Co. Model HLC-803D; RI-8) and M_ns of whole triblock copolymers. Indices of molecular weight distribution (M_w/M_n) equivalent to protonated polystyrene of centre polymers, arm polymers and triblock copolymers were determined by analytical g.p.c. The M_w/M_ns of arm polymers calculated with M_w and M_n values determined by light scattering and osmotic pressure measurements were slightly larger than those determined by g.p.c.

The characteristics of the samples thus determined are listed in *Table 1*. The degree of polymerization P is used instead of molecular weight M to avoid any confusion arising from the difference in M between deuterated and protonated styrenes. Molecular weights M_w and numbers of arms f of star-shaped polystyrenes are shown in *Table 2*. The deviation of the numbers of arms from integers suggests that the samples are mixtures of star-shaped polymers with different numbers of arms. However, the sedimentation pattern at 42 040 rev min^{-1} in 2-butanone at 25°C measured with a Beckmann Spinco model E analytical ultracentrifuge is very sharp (*Figure 2*), which indicates that the distribution of the number of arms is narrow.

Table 1 Characteristics of the centre units and arms of star-shaped polystyrenes

Sample		Degree of polymerization P		
		PVS	Polystyrene	P_w/P_n[a]
NF series				
Centre	NF-1	24		1.06
	NF-2	36		1.05
	NF-3	49		1.05
	NF-4	80		1.04
Arm			1810	1.06
LS series				
Triblock	LS-I	32	1630	1.08
	LS-O	45	1920	1.08
Arm			2150	1.06

[a] Determined by g.p.c.

Table 2 Molecular weights and radii of star-shaped polymers and calculated ratios

Sample	M_w ($\times 10^6$)	f	R_g (nm)	R_h (nm)	g_g^a	g_h^a	A_2 ($\times 10^{-4}$ ml mol g^{-1})
NF-1	1.18	6.3	35.7	29.0	1.97	2.84	1.98
NF-2	1.28	6.8	36.4	30.3	2.01	2.97	1.80
NF-3	1.85	9.9	36.2	31.6	2.00	3.09	1.54
NF-4	2.08	11.0	36.3	32.7	2.01	3.21	1.22
NF-arm	0.188	1	18.1	10.2	1	1	5.15
LS-I	4.82	21.7	49.4	46.0	2.24	3.87	0.749
LS-O	4.86	21.8	52.9	46.4	2.39	3.90	0.697
LS-arm	0.224	1	22.1	11.9	1	1	4.85

Figure 2 Sedimentation pattern of star-shaped polystyrene NF-1 in 2-butanone solution (0.2 wt%) at 42040 rev min^{-1}

Light scattering

Sample solutions were filtered through Millipore filter (nominal pore diameter 0.22 μm) into light scattering cells, followed by dilution with dust-free solvent to produce solutions of desired concentration. All cells containing solutions were subsequently sealed. Details of the light scattering spectrometer have been described elsewhere[11]. An argon ion laser operated at a wavelength of 488.0 nm was used as a light source. The photoelectron count autocorrelation function was measured by a Malvern correlator K7027.

All the light scattering data were obtained for toluene solution at 30°C. The methods of data analysis are the same as in a previous study of linear polystyrenes in the same solvent[11]. The M_w and radius of gyration R_g were calculated on the basis of the standard formulae for static light scattering. The translational diffusion coefficient D was computed from the average line width Γ obtained by the cumulant method[12], and was extrapolated to a vanishing concentration to obtain the value D_0 at infinite dilution which is related to the hydrodynamic radius R_h by the Einstein–Stokes equation.

RESULTS AND DISCUSSION

The R_g and R_h of star-shaped polystyrenes in toluene at 30°C are listed in *Table 2*. R_g is always larger than R_h. Star-shaped polymers in the NF series have arms of an equal length (the same degree of polymerization), which allows us to study directly the dependence of the radii R_g and R_h on the number of arms f. As seen in *Table 2*, R_g scarcely changes with f in the NF series. The difference between the largest and smallest values are less than experimental uncertainty. On the other hand, R_h increases obviously with f. R_h is more strongly dependent on f than R_g.

The centre of the star-shaped polymer used in the present experiment is not point-like but a short chain. The ratio of the degree of polymerization of a centre chain to that of an arm amounts to 0.044 in the highest case (sample NF-4). To make an estimate of the contribution from the centre chain to the radii, we calculated R_g and R_h for two cases where the centre polymer was neglected ('star') and where it was taken into account ('comb') based on a rather simple approximation. R_g and R_h are calculated by:

$$R_g^2 = \frac{1}{N^2} \sum_i \sum_j \langle r_{ij}^2 \rangle \tag{1}$$

$$R_h^{-1} = \frac{1}{N^2} \sum_i \sum_j \langle r_{ij}^{-1} \rangle \tag{2}$$

where N is the total number of segments in a polymer, and $\langle r_{ij}^2 \rangle$ is the mean square distance between two segments i and j. By assuming that $|r_{ij}|$ $(= (\langle r_{ij}^2 \rangle)^{1/2})$ can be expressed by a power law

$$|r_{ij}| = |i - j|^{\nu} a \tag{3}$$

where a is the segment length, and that the exponent ν is the same as that for R_g in a good solvent, i.e. $\nu = 0.6$, the ratio of the radius for a 'comb' to a 'star' is calculated numerically for two models (samples NF-4 and LS-2). Parameters used in these models and the calculated ratios are listed in *Table 3*. The contribution from the centre is small. The difference between 'comb' and 'star' is $<1\%$ for both R_g and R_h. It is a good approximation to neglect the centre chain of the present star-shaped polymers.

The ratio of the radius of a star-shaped polymer to that of the homologous linear polymer with the same molecular weight is generally considered to be a universal quantity which is independent of arm length (if not too short) and the system, and dependent on the number of arms and solvent goodness. This plays a central role in the study of star-shaped polymers as well as in the study of other kinds of branched polymers. The radius of the reference linear polymer with the same molecular weight as a star-shaped polymer is usually determined from interpolation of the data for several different molecular weights. Thus, some extra measurements are necessary to evaluate the ratio. For star-shaped polymers, another universal ratio of radius can be defined, namely, a free arm polymer can be used as a reference instead of a linear polymer with the same molecular weight. An arm

Table 3 Ratios of radii for comb- to star-shaped model polymers calculated by equations (1)–(3) with $\nu = 0.6$

f	P_{arm}	P_{centre}	R_g (comb)/R_g (star)	R_h (comb)/R_h (star)
11	1810	77	1.007	1.010
22	2160	44	1.004	1.006

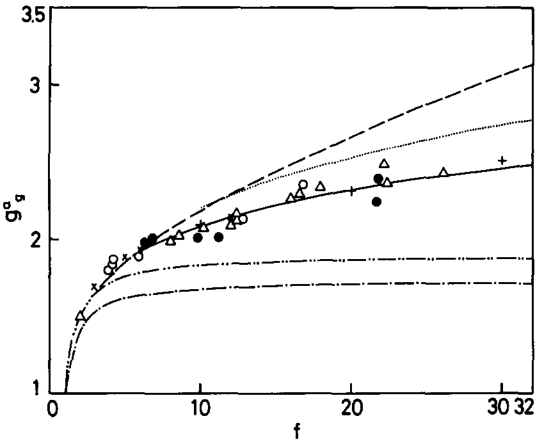

Figure 3 Ratio of radius of gyration g_g^a for a star-shaped polymer to its arm *versus* the number of arms f. Experimental: (●) present work; (○) polystyrene/toluene at 35°C[13,14]; (△) PIP/cyclohexane at 23°C[7]. Computer simulation: (×) Monte Carlo[15–17]; (+) molecular dynamics[18]. Theoretical: (–·–) Zimm–Stockmayer[19]; (–··–) modified Zimm-Stockmayer ($\nu = 0.6$); (––––) Miyake–Freed[2]; (——) Douglas–Freed[4,6]; (····) modified Flory[5]

polymer is quite easily obtained as a by-product in the synthetic process of a star-shaped polymer, and thus the radius of an arm polymer can be directly determined by a single measurement. For this reason, the latter ratio is mainly used in the present work. The notation g^a is given to the ratio to distinguish it from the ratio taken for the same molecular weight, for which the notation g is commonly used.

In *Table 2*, we list the g^a ratios for the radius of gyration $g_g^a \equiv R_g(\text{star})/R_g(\text{arm})$ and for the hydrodynamic radius $g_h^a \equiv R_h(\text{star})/R_h(\text{arm})$. Note that the first power of R_g is used in our definition of g_g^a, while the second power of R_g is commonly used in the definition of g_g. The ratio g_g^a is plotted in *Figure 3* against the number of arms. *Figure 3* also shows the results by Roovers *et al.*[13,14] for the same system at 35°C and the results of another good solvent system, polyisoprene (PIP)/ cyclohexane at 23°C, by Bauer *et al.*[7] All the experimental results for different polymers and arm lengths fall on a single curve, which indicates that g_g^a is a universal quantity. Universality of the ratio g_g^a is further checked by comparing with results from computer simulations. Since some of the simulation results are given only for the ratio $g_g \equiv R_g^2(\text{star})/R_g^2(\text{linear})$, we calculated g_g^a from g_g by the equation:

$$g_g^a = g_g^{1/2} f^{\nu} \qquad (4)$$

where ν is the exponent of molecular-weight dependence for the radius of gyration in a good solvent, for which we used a value of 0.6 or 0.588 depending on the referred work. Both Monte Carlo[15–17] (MC) and molecular dynamics[18] data fit in the experimental results over the entire f range investigated ($f < 30$), showing that universality holds for the ratio g_g^a.

Several theoretical predictions have been made for g_g (or g_g^a) ratios of star-shaped polymers and they are shown in *Figure 3* for comparison with experiment. Zimm and Stockmayer[19] (ZS) derived $g_g^a = [(3f-2)/f]^{1/2}$ based on Gaussian chain statistics in their pioneering work. The g_g^a ratio predicted by the ZS theory seriously deviates from experimental results. The discrepancy might be caused by the use of the value $\nu = 0.5$ for a good solvent system as suggested by the disagreement observed at $f = 2$. We made an attempt to calculate g_g^a numerically by equation (1) with a good solvent value $\nu = 0.6$ instead of $\nu = 0.5$. This simple modification for the ZS theory does not greatly improve agreement except for $f \leqslant 3$ as illustrated.

Miyake and Freed[2] (MF) calculated g_g^a by the renormalization group method to first order in the ε expansion ($\varepsilon = 4 - d$, where d is the dimension of space), and later Douglas and Freed[4,6] (DF) calculated g_g by combining the renormalization group theory and the two-parameter theory[20]. The agreement between the values calculated by the MF theory and the experimental results is good up to $f = 7$ but deteriorates as f increases: the theoretical values are consistently larger than experimental ones at higher fs. The renormalized two-parameter DF theory[4,6] improves agreement with experimental values very well over the MF renormalization group calculation. Here, g_g^a was evaluated, by using equation (4) with $\nu = 0.588$, from g_g calculated using the DF theory. The renormalization group theory is not expected to provide a good description for large f because the perturbation of the excluded volume interaction becomes large. Though Douglas *et al.*[5] estimate that the application of renormalization group theory should be restricted to $f < 12$, the agreement of the DF theory is excellent even at $f = 30$. At extremely large f, theoretical prediction does not agree well with the reported g_g. Roovers *et al.*[21] synthesized 263-arm star-shaped polybutadiene with arm molecular weight 4.23×10^4, and obtained $g_g = 0.0294$ ($g_g^a = 4.99$), while the DF theory gives $g_g = 0.0184$ ($g_g^a = 3.59$) at $f = 263$.

Since g_g^a is related to g_g by $g_g^a = g_g^{1/2} f^{1/2}$ in ZS theory, and $g_g^a = g_g^{1/2} f^{0.588}$ in DF theory, the discrepancy in g_g between these theories is different from the discrepancy in g_g^a. Therefore, it should be noted that agreement with experiment in the g_g ratio calculated by classical ZS theory is not so poor as expected from the discrepancy in g_g^a observed in *Figure 3*. ZS theory gives g_gs close to those given by DF theory: for example, $g_g = 0.160$ using ZS theory and $g_g = 0.173$ using DF theory at $f = 18$.

The blob theory by Daoud and Cotton[1] gives an exponent of f- dependence of g_g^a and is applicable to large f. The modified Flory theory[5] gives a prefactor together with the same exponent as the blob theory:

$$g_g^a \cong 1.39 f^{1/5}$$

Though the theoretical prediction is always larger than experimental results in the range of $f < 30$, the agreement is relatively good. For $f = 263$, modified Flory theory gives $g_g = 0.0225$, which is smaller than the experimental result by Roovers *et al.*[21] and the agreement is better than that by DF theory. To study the power relation further, we plotted our data together with the data of Roovers *et al.*[13,14] in a double logarithmic scale in *Figure 4*. Though the data show some scatter, the linear relation holds approximately. The line has a non-zero slope, which does not agree with the prediction by ZS theory. By fitting these data points, we obtain

$$g_g^a \cong 1.48 f^{0.145}$$

The exponent is smaller than that predicted by blob theory or modified Flory theory. The prefactor 1.48 is larger than the results by computer simulations in which the fixed exponent 1/5 is used (~ 1.35)[16,22]. If the exponent is fixed at 1/5, the prefactor is evaluated to be

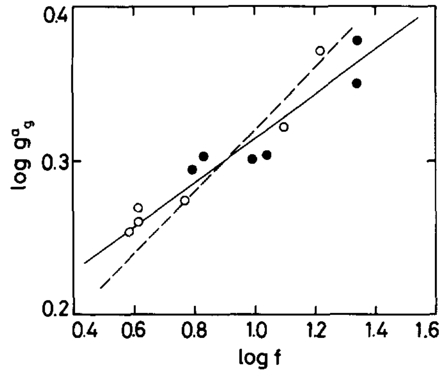

Figure 4 Log–log plot of g_g^a *versus* f: (●) present work; (○) polystyrene/toluene at 35°C[13,14]; (——) $g_g^a = 1.48f^{0.145}$; (– – –) $g_g^a = 1.32f^{1/5}$

1.32, which is compatible with the results by computer simulations.

Figure 5 shows g_h^a as a function of the number of arms, together with the results of sedimentation velocity measurements by Roovers *et al.*[13,14] for the same polystyrene/toluene system at 35°C and the results by Bauer *et al.*[7] for a PIP/cyclohexane system at 23°C. We omitted the data of short arm lengths (M_w of an arm $<4 \times 10^4$), because universal behaviour is not expected to hold for very short arms. The discrepancy observed between our data and those by Roovers *et al.* might be caused by an error in evaluating R_h for the arms of their samples. We calculated R_h of the arms by their formulation for the M_w dependence of R_h for linear polystyrenes given in the same references. The M_w of the arms might be out of the applicable range of the formula, because R_h for the arm in our NF series calculated by the formula is $\sim 15\%$ larger than the actual value.

If the draining effect depends on the number of arms and the length of an arm, g_h^a or g_h would depend on the system. Thus, it is not certain that the universality holds for the ratio of hydrodynamic radius. Although *Figure 5* shows relatively large scatter compared with *Figure 3*, data points for two good solvent systems (polystyrene/toluene and PIP/cyclohexane) approximately fall on a single curve. In addition, no clear indication of arm-length dependence of g_h^a is observed. This suggests that the ratio of the hydrodynamic radius is not sensitive to the system used.

There are still only a few computer simulations for hydrodynamic quantities of star-shaped polymers. Available MC results[15,17,23] are shown in *Figure 5*. Here, we calculated g_h^a from g_h ($\equiv R_h(\text{star})/R_h(\text{linear})$) by:

$$g_h^a = g_h f^{\nu} \tag{4a}$$

with $\nu = 0.588$. Although the experimentally obtained value for the exponent ν of the molecular weight dependence for R_h is slightly smaller than that for R_g, it is reported that computer simulation data of R_h of star-shaped polymers are compatible with $\nu = 0.588$ at large molecular weights[22]. The computer simulation data at $f = 6$ by different workers agree well, and are also in fair agreement with experimental results. The MC data for $f = 12$ and 18 obviously deviate from experimental data. These MC data were obtained by extrapolating g_hs for the star-shaped polymers with arms made up of only one to three segments to the value for that with infinitely long arms. Thus the observed difference can be caused due to error in the extremely long extrapolation, and it is not certain that universality of the ratio of hydrodynamic radius fails.

No two-parameter calculations for hydrodynamic properties are available for star-shaped polymers even in the preaveraging approximation. Thus the renormalized two-parameter (RTP) theory cannot be applied to the evaluation of g_h. Only classical theory is available for g_h at present. Stockmayer and Fixman[24] (SF) calculated g_h for the case of strong hydrodynamic interaction based on Gaussian chain statistics. Their result seriously deviates from experimental results as seen in *Figure 5*. Predicted curves are smaller than experimental values, showing the same tendency as in the g_g^a *versus* f relation. The simple modification in which $\nu = 0.6$ was used to calculate R_h using equations (2) and (3) improves agreement at small fs, but the modified calculation still seriously underestimates g_h at high fs. As pointed out in a previous section, the classical Gaussian calculation gave a much better prediction for the g ratio than the g^a ratio in the case of R_g. We also studied it in the case of R_h. We calculated $g_h f^{0.588}$ by SF theory ($g_h = f^{1/2}/[2^{1/2}(f-1)+(2-f)]$) and obtained the result shown in *Figure 5*. The agreement with experimental data is better than g_h^a, i.e. $g_h f^{0.5}$, but still deviates seriously at high fs. The agreement in g_h is not so good as in g_g.

The ratios g_h^a for the polystyrene/toluene system are plotted against f on a logarithmic scale in *Figure 6* to show the power relation. Least-squares fitting gives:

$$g_h^a \cong 1.51 f^{0.29} \qquad \text{(all data points)}$$

Since there is a problem in evaluating R_h of the arms as mentioned above, we also fit the data by Roovers *et al.*[13,14] and our data separately and obtain:

$$g_h^a \sim f^{0.25 \pm 0.01} \qquad (6 < f < 22, \text{ this work})$$

$$g_h^a \sim f^{0.32 \pm 0.02} \qquad (3 \leqslant f \leqslant 18, \text{ Roovers } et\ al.)$$

The difference between these two exponents is not small and therefore the uncertainty of the value is relatively large. It is nevertheless apparent that g_h^a depends on the number of arms more strongly than g_g^a, which has an exponent of <0.2.

Figure 7 shows the ratio of the radius of gyration to the hydrodynamic radius ρ ($= R_g/R_h$) against f. Since

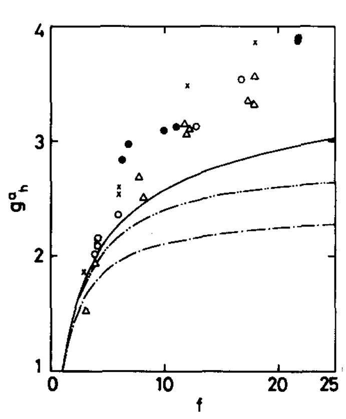

Figure 5 Ratio of hydrodynamic radius g_h^a for a star-shaped polymer to its arm *versus* number of arms f. Experimental: (●) present work; (○) polystyrene/toluene at 35°C[13,14]; (△) PIP/cyclohexane at 23°C[7]. Computer simulation: (×) Monte Carlo[15,17,23]. Theoretical: (–·–) Stockmayer–Fixman[24]; (–··–) modified Stockmayer–Fixman ($\nu = 0.6$); (——) $g_h f^{0.588}$

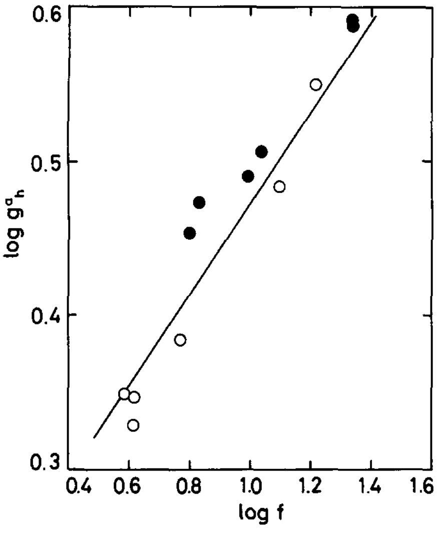

Figure 6 Log-log plot of g_h^a *versus* f: (●) present work; (○) polystyrene/toluene at 35°C[13,14]; (——) $g_h^a = 1.51f^{0.29}$

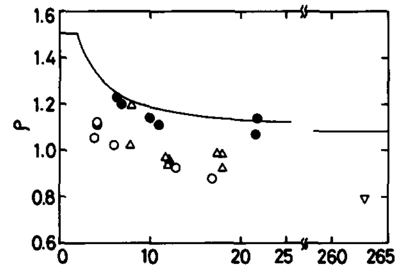

Figure 7 Ratio of radius of gyration to hydrodynamic radius ρ *versus* number of arms f. Experimental: (●) present work; (○) polystyrene/toluene at 35°C[13,14]; (△) PIP/cyclohexane at 23°C[7]; (▽) polybutadiene/cyclohexane at 30°C[21]. Theoretical: (——) Burchard *et al.*[25]

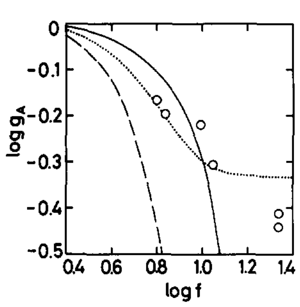

Figure 8 Log-log plot of the ratio of the second virial coefficient g_A for a star-shaped polymer to a linear polymer with the same molecular weight *versus* the number of arms f. Experimental: (○) polystyrene in toluene at 30°C. Theoretical: renormalization group calculation (---) to ε (ref. 2); (···) to ε^2 (ref. 3); (——) RTP theory[4]

it is known that ρ depends on polymers and molecular weights even in linear polymers, we cannot expect universal behaviour of ρ in star-shaped polymers either. Actually, the scattering of data points is larger than that observed in g_g^a or g_h^a. The curve predicted by classical theory[25] for the non-free-draining limit reproduces the trend of the dependence on f, but is always higher than observed. The asymptotic value predicted by theory is larger than unity, while the experimental ρ at $f = 263$ has a value close to that of a hard sphere.

The universal ratio can be defined for a quantity other than molecular dimensions. *Figure 8* shows the ratio of the second virial coefficient A_2, $g_A \equiv A_2(\text{star})/A_2(\text{linear})$, as a function of f in a logarithmic scale. A_2 of linear polystyrene in toluene was evaluated from the data in reference 11. Fitting to a power representation gives:

$$g_A \cong 1.65f^{-0.480}$$

Using the renormalization group method, g_A has been calculated to the first order in ε by Miyake and Freed[2] and to the second order by Douglas and Freed[3]. As seen in *Figure 8*, the second-order calculation improves the agreement with experimental data very well over the first-order calculation, but deviates seriously at $f > 12$. The RTP theory[4,6] has also been applied to the calculation of g_A. Agreement between experimental data and the RTP theory is relatively good at lower fs ($\leqslant 10$), but seriously deteriorates as f increases. The RTP theory gives an unphysical negative g_A at $f > 16$. In contrast to g_g^a, applicability of the RTP theory for A_2 is limited to relatively small fs.

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