

Viscosity and Steady-State Compliance of Multi-Branched Star Polystyrenes[†]

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(Received October 7, 1985)

ABSTRACT: Reductions of molecular weight dependences of the zero-shear viscosity η_0 and the steady-state compliance J_e^0 for multi-branched star polystyrenes with different numbers ($P=7\sim 40$) and molecular weights ($M_s=1.3\sim 20\times 10^4$) of branches as well as those of small-number (six or less) branched polystyrenes and linear ones have been investigated. The reduction methods of η_0 and J_e^0 ever established both theoretically and experimentally for small-number branched star polymers could not be applied to multi-branched star polymers. We tried to reduce the data of η_0 and J_e^0 for multi-branched star polymers by corrected molecular weights by considering the expansion of molecules. In the course of discussions we proposed a new method to estimate the unperturbed dimensions of star polymers from the rheological measurements.

KEY WORDS Polystyrene / Star Branched Polymers / Viscosity / Steady-State Compliance / Molecular Weight Dependence /

In the terminal or flow zone, the viscoelastic behavior of polymer melts can be characterized by the zero-shear viscosity η_0 and the steady-state compliance J_e^0 .^{1,2} A lot of experimental studies on the viscoelastic properties for star-shaped polymers having the number of branches six or less have been carried out³⁻²⁰ and have established the molecular weight dependences of η_0 and J_e^0 , which quantitatively agree with recent theories.²¹⁻²³

In the previous paper,²⁴ the viscoelastic properties of multi-branched star polystyrenes having a variety of number (P) and molecular weight (M_s) of branches were measured in wide ranges of temperature and frequency, and the effects of temperature, total molecular weight M , M_s , and P were investigated. In this paper, the multi-branched star polymer means that having more than seven branches in a molecule.

Mean square radius of gyration of multi-

branched star polystyrene prepared by coupling narrow-distribution polystyryl anions with divinylbenzene (DVB) was found to be larger than that the random-walk model predicts,^{25,26} because of a microgel nodule at the center of molecule.^{25,27-31} In recent studies,^{32,33} however, it was found that the extra expansion of multi-branched star polymer is due to the effect of increased segment density near its center. The non-Gaussian distribution of the chain segments not only makes the molecules expanded but also reduces flexibility of chain near the central branch point. This effect gives rise to a *core* formed at the center of molecule, which behaves rheologically like a nodule. Both the extra expansion and the reduced flexibility at the center of multi-branched star molecule necessarily affect the rheological properties of the melts.

This paper describes reduction of the mo-

[†] Rheological Properties of Anionic Polystyrenes XII.

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lecular weight dependences of zero-shear viscosity and steady-state compliance for multi-branched star polystyrenes by use of the data reported previously.²⁴ The reduction method proposed here was made in consideration of the difference in expansions of star polymers having six or less branches and multi-branched ones. Moreover, we propose a new rheological method for determination of the mean square radius of gyration of multi-branched star molecules.

EXPERIMENTAL

Star-branched samples have been prepared by copolymerization of narrow-distribution polystyryl anions with DVB. Polymer preparation and characterization were described in detail in our previous paper.²⁴ Table I shows the molecular characteristics of the samples employed here. The measurements of rheological properties of star polymers were carried out with a cylinder type rheometer.^{15-17,22} The numerical values of the zero-shear viscosity η_0 and the steady-state compliance J_e^0 at the fractional free volume $f=0.0608$ for multi-branched star polystyrenes²⁴ are tabulated in Table II. All the data to be shown in this paper are those in the iso-free-volume state.

RESULTS AND DISCUSSION

Zero-Shear Viscosity

In present section, we try to find the most reasonable method to reduce the molecular weight dependence of zero-shear viscosity by corrected molecular weights for multi-branched star polystyrenes. The trials have been carried out by use of (i) the span molecular weight, (ii) the mean-square radius of gyration calculated by the Gaussian distribution of the segments, (iii) the intrinsic viscosity at θ -temperature of corresponding linear polymers, and (iv) the experimentally determined radius of gyration of star molecules in the molten state. Discussions given

Table I. Characteristics of multi-branched star polystyrenes

Sample	M_w^a $\times 10^{-4}$	M_w/M_n^b	M_s^c $\times 10^{-4}$	P^d	$[\eta]^e$ dl g ⁻¹
LM1	262	1.19	5.68	38.7	0.279
LM2	234	1.21	6.01	32.1	0.269
LM3	86.1	1.17	5.02	14.7	0.282
LM4	148	1.19	5.62	22.1	0.280
LM5	189	1.21	5.25	29.7	0.274
LM6	95.7	1.19	6.23	12.9	0.320
LM7	44.6	1.30	5.50	7.2	0.276
LM8	26.3	1.18	1.17	19.1	0.139
LM9	94.9	1.20	3.43	23.1	0.225
LM10	144	1.16	8.21	15.1	0.345
LM11	189	1.18	11.3	14.2	0.404
LM12	302	1.13	17.9	14.9	0.474

^a Weight-average molecular weight of star polymer.

^b Molecular weight distribution of star polymer.

^c Number-average molecular weight of a branch.

^d $P = M_n(\text{star})/M_n(\text{branch})$.

^e Measured in cyclohexane at 34.5°C.

Table II. Zero-shear viscosity η_0 and steady-state compliance J_e^0 at $f=0.0608$ for multi-branched star polystyrenes.

Sample	$M_w \times 10^{-4}$	η_0 poises	J_e^0 cm ² dyn ⁻¹
LM1	262	2.76×10^7	8.7×10^{-6}
LM2	234	1.36×10^7	6.0×10^{-6}
LM3	86.1	4.23×10^6	2.43×10^{-6}
LM4	148	7.6×10^6	4.9×10^{-6}
LM5	189	6.2×10^6	6.2×10^{-6}
LM6	95.7	8.6×10^6	3.5×10^{-6}
LM7	44.6	2.50×10^6	1.60×10^{-6}
LM8	26.3	5.6×10^4	1.9×10^{-6}
LM9	94.9	1.48×10^6	4.1×10^{-6}
LM10	144	1.97×10^7	4.3×10^{-6}
LM11	189	9.1×10^7	5.2×10^{-6}
LM12	302	7.0×10^8	9.6×10^{-6}

here are based upon a few reasonable assumptions; (1) the zero-shear viscosity can be determined by the radius of gyration of molecules even in the entanglement region, unless the total molecular weights of star-branched polymers are high enough to enter into the enhancement region of viscosity. (2)

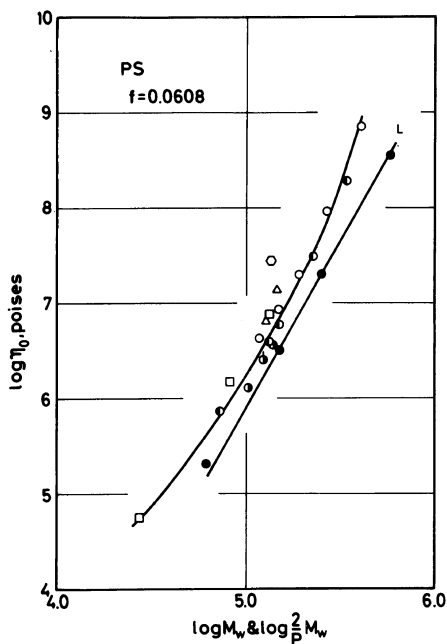


Figure 1. η_0 logarithmically plotted against the span molecular weight $(2/p)M_w = 2M_s$ for star-shaped polystyrenes in the iso-free-volume state $f=0,0608$; ● linear polymers; ● $P \approx 3.5$; ● $P \approx 6$; ● $P \approx 7$; ○ $P \approx 15$; □ $P \approx 20$; △ $P \approx 30$; ○ $P \approx 40$.

Dimensions of multi-branched star molecules in molten state are the same as those at θ -condition in dilute solutions.

(i) *Reduction by Span Molecular Weight*

Doi and Kuzuu (DK)²¹ and Pearson and Helfand (PH)²² presented theories on the rheological properties of star-shaped polymers with P branches of equal length based on the tube model. Those theories give an exponential molecular weight dependence of η_0 , which can be expressed by a function of the molecular weight per branch, $M_s = M/P$.

$$\eta_0 \propto (M_s/M_e)^a \exp(v' M_s/M_e) \quad (1)$$

where M_e is the average molecular weight between entanglements and v' a numerical factor. The exponent a is 2 for DK theory and 1/2 for PH theory.

To test the principle, η_0 for linear and star polystyrenes are plotted against the span molecular weight $2M_w/P = 2M_s$ in Figure 1. Here

η_0 was evaluated by the following equation:

$$\eta_0 = \lim_{\omega \rightarrow 0} G''/\omega \quad (2)$$

$2M_s$ corresponds to an end-to-end contour length of the star-shaped polymer chains. Open circles indicate star polymers having about 15 branches, squares those having about 20 branches, triangles those having about 30 branches, right black circles those having six branches, and black circles linear polystyrenes. The left black circles represent mixtures of three- and four-branched polymers. All of the plots for star polystyrenes with various P except $P=40$ seem to mount on a single curve, on which no straight portion can be observed. Bauer *et al.*³⁴ reported a similar result for star-shaped polyisoprenes with $P=8$ and 12. These experimental results strongly support the theoretical prediction derived by applications of the tube model to star molecules.

(ii) *Reduction by the Gaussian Mean-Square Radius of Gyration*

Another approach to the reduction principle for η_0 of branched polymers is that by the radius of gyration. According to Bueche's theory,³⁵ if branches are long enough to become engaged in interchain entanglements and a molecule in molten state has the Gaussian distribution of segments about the mass center, the ratio of the zero-shear viscosity of the star polymer to that of the corresponding linear polymer depends only upon the radius of gyration.

$$\eta_0 = f(g_s^2 M) \quad (3)$$

where g_s^2 is defined by the ratio of the mean square radius of gyration $\langle s^2 \rangle$ of a branched polymer to that of a corresponding linear polymer with the same molecular weight in the θ -condition. The g_s^2 was first theoretically calculated by Zimm and Stockmayer³⁶ for random-flight chains with no excluded volume effect between segments and is given by the following equation for regular stars having P branches per molecule.

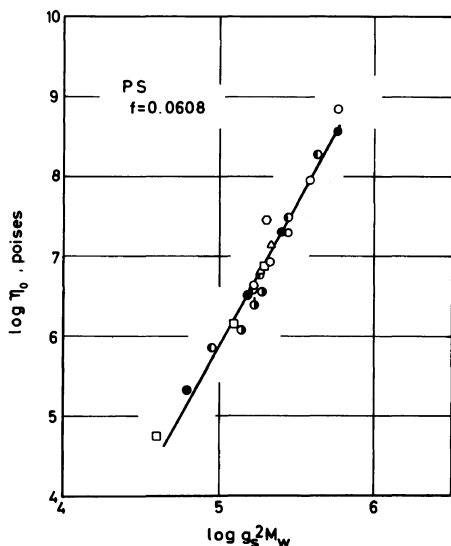


Figure 2. η_0 logarithmically plotted against the reduced molecular weight $g_s^2 M_w$ for star-shaped polystyrenes at $f=0.0608$. Values of g_s^2 were calculated from eq 4. The marks are the same as those in Figure 1.

$$g_s^2 = \langle s^2 \rangle_b / \langle s^2 \rangle_l = (3P - 2) / P^2 \quad (4)$$

where subscripts b and l denote the branched and linear polymers, respectively.

In Figure 2, the zero-shear viscosity η_0 for linear and star polystyrenes are logarithmically plotted against $g_s^2 M_w$, using g_s -values calculated from eq 4, to be compared with Bueche's theory. The marks are same as those in Figure 1. As is seen from this figure, the plots for star polystyrenes with various number of branches seem to coincide well with those for linear polymers which are expressed by the closed circles and the straight line. This coincidence, however, might be deceptive by the following reason. It was reported that experimental values (for example, obtained by light scattering method) of g_s^2 for multi-branched polymers are larger than values calculated from eq 4 at higher P than nine,^{25,26,32,33} as will be shown in Figure 5. This effect is caused by the extra expansion of chains according to the non-Gaussian character of segment distribution at the center of molecule. Therefore, when experimental values are used instead of g_s^2 from

eq 4, $\log \eta_0$ vs. $\log g_s^2 M_w$ plots for star polymers having P higher than nine should deviate to the right side of the linear line. Thus, it can be concluded that the good reduction of $\log \eta_0$ vs. $\log g_s^2 M_w$ plots for multi-branched polymers with those for linear ones, as is seen in Figure 2, is just apparent.

(iii) *Reduction by Intrinsic Viscosity*

Some calculations of the intrinsic viscosity of branched polymers were made by Zimm and Kilb,³⁷ taking into account of the hydrodynamic interaction between polymer chains and using the Gaussian model. The intrinsic viscosity of branched polymers is conveniently expressed by

$$g_\eta^3 = [\eta]_b / [\eta]_l \quad (5)$$

where $[\eta]_b$ and $[\eta]_l$ are the intrinsic viscosity of branched and linear polymers having the same molecular weight, respectively. For regular star-shaped polymers under the non-free-draining condition, no exact closed expression could be derived for g_η^3 but the result of ZK theory can be approximately written as

$$g_s = g_\eta^3 \quad (6)$$

If the Zimm-Kilb relationship is valid for regular stars and $[\eta]$ measured in theta solvent is proportional to $M^{1/2}$, η_0 can be expressed by following equations:

$$\eta_0 = f(g_s^2 M) = h([\eta]^2) \quad (7)$$

In order to test the validity of eq 7, we plotted η_0 for star polystyrenes against the square of the intrinsic viscosity $[\eta]$ measured at 34.5°C in Figure 3. As is seen from this figure, η_0 of star polymers having 3–6 branches agrees well with that of linear polymers (closed circles) at low molecular weight, but it shows the enhancement at the molecular weights of branches, M_s , higher than $7-8 \times 10^4$. Similar results were reported by Graessley and co-workers for four- and six-branched polyisoprenes⁷ and polystyrenes,⁹ by Hadjichristidis *et al.* for four- and six-branched polyisoprene solutions,⁶ by Rochefort *et al.* for star-

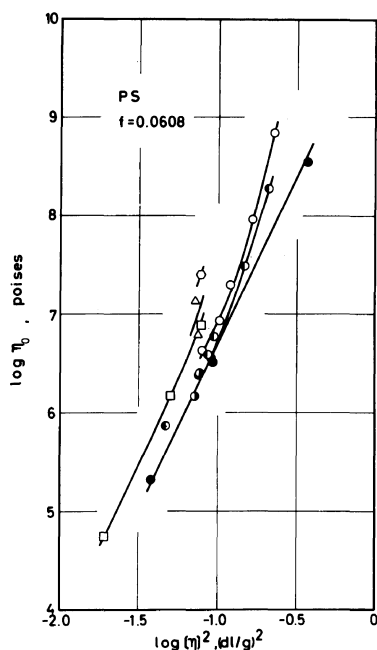


Figure 3. η_0 logarithmically plotted against the square of the intrinsic viscosity $[\eta]$ measured at 34.5°C for star-shaped polystyrenes. The marks are the same as those in Figure 1.

branched polybutadienes,⁸ and by Raju *et al.* for star-shaped hydrogenated polybutadienes.¹¹

On the other hand, η_0 of star polymers having more than 13 branches is higher than that of linear polymers even at M_s lower than 8×10^4 ; the more branches of equal length a polymer has, the higher the viscosity becomes. Moreover, for multi-branched polymers with M_s higher than 8×10^4 , the viscosity enhancement is observed as in the star polymers with six or less branches and M_s above $3-4 M_e$.^{3,7,9,25} At constant P , $\log \eta_0$ vs. $\log [\eta]^2$ lines for multi-branched polymers with M_s lower than 8×10^4 are almost parallel with that for linear polymers, irrespective of number of branches. It should be pointed out again that the inconsistency of eq 7 revealed between Figure 2 and Figure 3 is caused also by the extra expansion of multi-branched star molecules noted before.

$[\eta]$ used in this study was measured at a

constant temperature (34.5°C; θ -temperature for linear polystyrene in cyclohexane) rather than real theta temperature θ_{A2} , at which the second virial coefficient $A_2=0$. It is well known that θ_{A2} for multi-branched star polymers is much lower than that for linear ones.^{6,25,26,32,38-40} Accordingly, $[\eta]$ measured at 34.5°C must be higher than that measured at θ_{A2} , and the deviation of $\log \eta_0$ vs. $\log [\eta]^2$ curve for multi-branched polymers from that for linear ones must become further large, when $[\eta]$ measured at θ_{A2} is used. This indicates that the $\log \eta_0$ vs. $\log [\eta]$ curve for multi-branched polymers cannot be superposed on that for linear polymers and star polymers having six or less branches.

(iv) *Reduction Based on Experimental Results ever Obtained for $P \leq 6$.*

Recent experimental results^{6,18,25,40} have shown that the relation of $g_s = g_\eta^{2.5}$, instead of $g_s = g_\eta^3$, holds for star-shaped polymers with P below six. Moreover, a successful superposition can be attained by plotting $\log \eta_0$ against $\log [\eta]^2$ for branched polymers with P below six and linear ones in the absence of viscosity enhancement,^{6,7,9,10,18,25} as also shown in Figure 3. Thus, the correlation using $g_s^{2.4} M_w$, instead of $g_s^2 M_w$ gives close agreement between branched and linear polymers.

$$\eta_0 = F(g_s^{2.4} M_w) \quad (8)$$

In Figure 4, η_0 is logarithmically plotted against $g_s^{2.4} M_w$ for multi-branched star polystyrenes. The marks are same as those in Figure 1. As is evident from this figure, η_0 of branched polymers having P below six (left and right black circles) agrees well with that for linear polymers (closed circles) at low molecular weights. On the other hand, η_0 of star polymers having P higher than 13 is higher than that of the corresponding linear polymers. Moreover, the more branches of equal length a polymer has, the larger the discrepancy becomes. $\log \eta_0$ vs. $\log g_s^{2.4} M_w$ curves for multi-branched polymers having constant P are almost parallel with that for

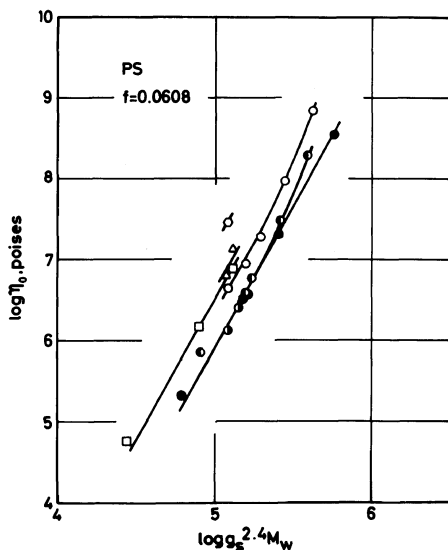


Figure 4. η_0 logarithmically plotted against the reduced molecular weight $g_s^{2.4}M_w$ for star-shaped polystyrenes, using eq 4 for g_s^2 . The marks are the same as those in Figure 1.

linear polymers at low molecular weights ($M_s = 8 \times 10^4$), disregarding the number of branches. But the separation becomes larger as the number of branches increases. This implies that the correction of molecular weight by g_s -values is excess. In order to obtain a good agreement of η_0 curves for multi-branched polymers with that for linear ones, correction factors larger than g_s should be employed.

Here, we assume that the deviation of the values for $P \geq 13$ in Figure 4 from the line for linear polymers is caused by the extra expansion of multi-branched molecules, and that η_0 can be reduced by $g^{2.4}M_w$, using a real branching factor $g^{2.4}$ resulting from the non-Gaussian character of the chain near the center of molecule, instead of $g_s^{2.4}$ calculated by eq 4. Such correction values can be estimated as follows. The weight-average molecular weight of a linear polymer with the same η_0 as a branched polymer, M_w^* , is read from $\log \eta_0$ vs. $\log M_w$ curve for the linear polymer. Then, the ratio of M_w^* to M_w for the branched polymer is

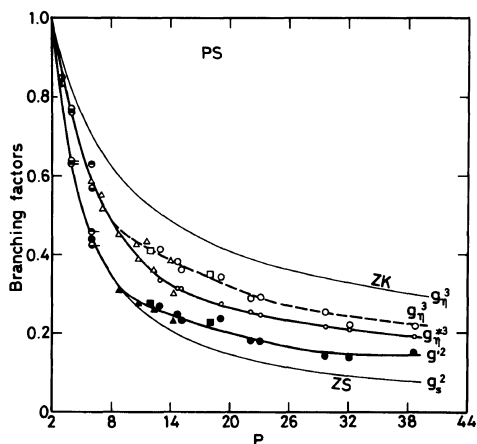


Figure 5. Branching factors g_s^2 , $g^{2.4}$, g_n^3 , and g_n^{*3} plotted against the number of branches P for star-shaped polystyrenes. ZS³⁶ and ZK³⁷ lines are theoretical ones by eq 4 and 6, respectively. Large open circles indicate g_n^3 estimated from eq 5, using $[\eta]_0$ obtained at 34.5°C and $[\eta]$ calculated by eq 10. Small open circles indicate g_n^3 estimated by using eq 9 and 10, and large closed circles, $g^{2.4}$ estimated from η_0 vs. $g_s^{2.4}M_w$ curves (see text). The other marks represent experimental values at or near θ_{A2} reported by various authors (● ref 42; ○ ref 43; ⊙, ⊖ ref 40; ⊕, ⊖ ref 39; △, ▲ ref 26; □, ■ ref 33).

obtained. This ratio will give $g^{2.4}$. The four highest η_0 data (two ○'s and two ●'s in Figure 4) were excluded from the procedure, because the molecular weights of the samples obviously are in the enhancement region.

In Figure 5, $g^{2.4}$ determined for star-shaped polystyrenes (large closed circles) are plotted against the number of branches P . In this figure, g_s^2 values (⊙, ⊖, ▲, ■) determined absolutely by various authors^{26,33,39,40} for star-shaped polystyrenes at or near θ_{A2} are also plotted. As is seen in this figure, values of $g^{2.4}$ for star polymers having 6 to 18 branches agree well with experimental values of g_s^2 . This means that g_s^2 for star polymers having P lower than 18 can be obtained by measurement of η_0 , without measuring the mean square radius of gyration $\langle s^2 \rangle$. At P higher than 10, the absolutely determined values of g_s^2 become higher than theoretical ones of g_s^2 (lower thin line) obtained by eq 4. Noda *et al.*⁴¹ reported

similar results that experimental values of g_s^2 for comb-shaped polystyrenes are larger than theoretical ones of g_s^2 , when number of branches is high. Experimental test of g_s^2 for star polystyrenes with P higher than 18 has not been reported yet, but we believe that g^2 determined here by the superposition of zero-shear viscosity correspond to experimental values of g_s^2 for multi-branched polymers at θ_{A2} .

Branching Factors for Multi-Branched Star Polystyrenes

In Figure 5, g_η^3 (large open circles) and g_η^{*3} (small open circles) are also plotted against P , where large open circles indicate values of g_η^3 obtained by using $[\eta]_b$ at 34.5°C and small open circles represent values of g_η^{*3} ($=[\eta]_{*,\theta}/[\eta]_b$) obtained by the use of $[\eta]_{*,\theta}$ calculated from the following equation reported by Zilliox,²⁶ who measured the intrinsic viscosity in cyclohexane at the temperature θ_{A2} for multi-branched star polystyrenes with P higher than 10.

$$[\eta]_{*,\theta} = 1.25[\eta]_{s,\theta} \quad (9)$$

Here, $[\eta]_{s,\theta}$ indicates the intrinsic viscosity at θ_{A2} for parent polymers and is proposed by the following equation,¹⁸

$$[\eta]_{s,\theta} = (7.9 \times 10^{-4})M_w^{0.5} \quad (10)$$

g_η^3 values (●, ○, ⊙, ⊖, △, and □) obtained by various authors^{26,33,39,40,42,43} for star-shaped polystyrenes at or near θ_{A2} are also plotted in the figure. As is seen from this figure, g_η^3 values obtained in this study (at 34.5°C; open circles) and results by Roovers *et al.*³³ (at 35°C; open squares) look higher than experimental values of g_η^3 obtained by using $[\eta]_b$ at θ_{A2} (triangles)²⁶ in the range of P above 10, though two triangles locate somewhat high. As mentioned before, intrinsic viscosity measurements were carried out at the other temperature (34.5°C) than θ_{A2} to result in somewhat higher $[\eta]_b$. Therefore, it is better to employ g_η^{*3} obtained by using

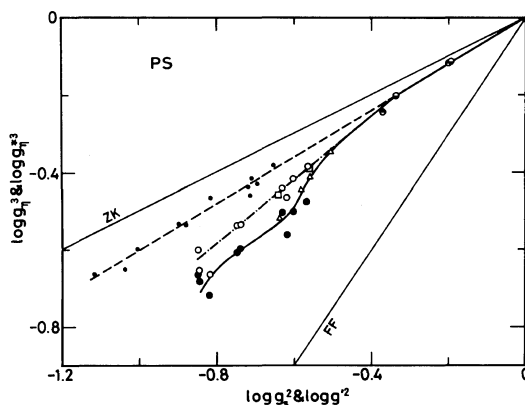


Figure 6. Relation between g_s^3 and g^2 , and between g_η^{*3} and g^2 for star-shaped polystyrenes. Open circles indicate values estimated from g_η^3 obtained by using $[\eta]$ at 34.5°C and from g^2 , and closed circles those estimated from g_η^{*3} and g^2 . The other marks represent experimental values at or near θ_{A2} reported by various authors (● ref 39; ⊙ ref 40; △ ref 26; □ ref 33).

$[\eta]_{*,\theta}$ than to employ g_η^3 obtained by using $[\eta]_b$ at 34.5°C. As is seen from Figure 5, the line drawn for the small open circles coincides better with some of the experimental values at θ_{A2} and is more smoothly connected with the line for $P < 9$ than that for the large open circles do. The Zimm-Kilb theory (upper thin line) does not hold at all for entire range of P .

The relations between g_η^3 and g^2 , and between g_η^{*3} and g^2 for multi-branched polystyrenes is shown in Figure 6, where open circles indicate values estimated from g_η^3 obtained using $[\eta]$ at 34.5°C and g^2 , and closed circles, values estimated from g_η^{*3} obtained by using $[\eta]_{*,\theta}$ and g^2 . Here g^2 was estimated from relation between η_0 and $g_s^{2.4}M_w$ for star and linear polymers mentioned above. Data for star polymers at or near θ_{A2} reported by various authors^{26,33,39,40} were also plotted by upper and down black circles, squares, and triangles in the same figure. ZK and FF curves represent relation of $g_s = g_\eta^3$ and $g_s = g_\eta$, respectively. A slope of a broken line in this figure is equal to 0.6 and the relation for star polymers with $P \leq 6$ can well be represented by

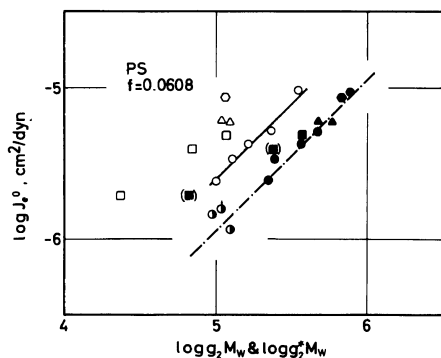


Figure 7. The steady-state compliance J_e^0 logarithmically plotted against the reduced molecular weight $g_2 M_w$ or $g_s^* M_w$ for star-shaped polystyrenes. The marks are the same as those in Figure 1. Closed marks indicate results estimated by using g_s^* obtained by substituting $P=7$ into eq 12, and a chain line shows the prediction of the extended Rouse theory for linear polymers.

$g_s = g_\eta^{2.5}$. However, with increasing number of branches, deviation from the relation of $g_s = g_\eta^{2.5}$ becomes larger (triangles and squares), though values reported by Zilliox (triangles)²⁶ are lower than those reported by Roovers *et al.* (squares).³³ On the other hand, comparing results obtained in this study (open and closed circles) with those absolutely measured near θ -temperature (triangles and squares), open circles coincide well with squares at the same g_s^2 and fit on a chain line with a slope of 0.82 to give a relation, $g_s \propto g_\eta^{1.83}$, while closed circles agree almost with triangles at the $\log g_s^2$ of about -0.6 . Experimental test for star-shaped polystyrenes with P higher than 18 has not been reported yet, and the relation between g_s^2 and g_η^3 is not clear for star-shaped polymers having P higher than 18. We should remark here that plots of g_η^3 (at 34.5°C) against g_s^2 (from eq 4) apparently satisfy²⁴ the real relation between g_η^3 (at θ -temperature) and g_s^2 obtained for $P \leq 6$, as shown by small closed circles and broken line in Figure 6.

Steady-State Compliance

A theory for the viscoelastic properties of dilute solutions of star polymers having vari-

ous types of topology has been first presented by Ham,⁴⁴ who assumed hydrodynamic interaction and entanglement couplings to be negligible, corresponding to the Rouse theory for linear polymers.⁴⁵ For monodisperse regular stars, Ham's theory gives

$$J_e^0 = 0.4 g_2 M / cRT \quad \text{for } \eta_b \gg \eta_s \quad (11)$$

where η_s is the solvent viscosity, c the concentration of polymer, R the gas constant, T the absolute temperature, and

$$g_2 = (15P - 14) / (3P - 2)^2 \quad (12)$$

Recent experimental results^{5,7,9,10,12,18} on star polymers having P smaller than six show that the relation between the steady-state compliance J_e^0 and M can well be described by the Rouse-Ham theory.^{44,45} Therefore, it is interesting to test the validity of this theory for multi-branched polymers with many branches.

In Figure 7, J_e^0 of various star polystyrenes is plotted against $g_2 M_w$ in order to compare with theoretical calculations based on Ham model⁴⁴ represented by eq 11 and 12. Here, J_e^0 is defined as follows:

$$J_e^0 = \lim_{\omega \rightarrow 0} G' / \omega^2 \eta_0^2 \quad (13)$$

Open marks and right black circles in this figure are same as those in Figure 1. The chain line indicates prediction from the extended Rouse theory for linear polymers.¹

$$J_e^0 = 0.4 M / cRT \quad (14)$$

As is evident from this figure, plots of $\log J_e^0$ vs. $\log g_2 M_w$ for six- and seven-branched polystyrenes (right black circles) fit on the chain line, though the Ham theory is applied only to polymers which are too short to participate in entanglement couplings. Yasuda *et al.*²⁰ reported that there is no difference between J_{eR}^0 for concentrated solutions of linear polystyrenes and those of star ones with P ranging from 6.4 to 8, where J_{eR}^0 is the reduced steady-state compliance defined for star polymers as follows:

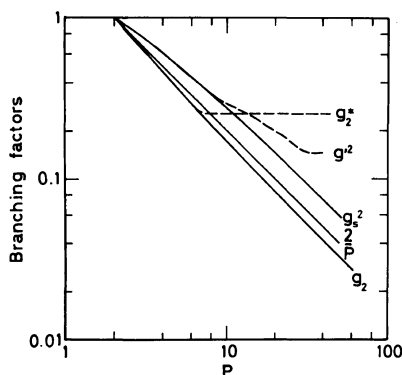


Figure 8. Branching factors $2/p$, g_2^* , g^2 , g_n^3 and g_n^{*3} plotted against the number of branches P for star-shaped polymers.

$$J_{\text{CR}}^0 = J_e^0 cRT/g_2 M \quad (15)$$

Thus, plots of $\log J_e^0$ against $\log g_2 M_w$ for concentrated solutions of star polymers reported by Yasuda *et al.* agree with the extended Rouse theory for linear polymers. As can be seen from Figure 7, however, the plot of J_e^0 for star polymers with P of about 15 (open circles) can be represented by a straight line almost parallel with but deviated from the theoretical chain line. Experimental results for star polymers with more branches (Δ , \square , \circ) deviate more from the theoretical line, and the deviation becomes larger as the number of branches increases.

According to the DK or the PH theory, the molecular weight dependence of J_e^0 for star-shaped polymers can be expressed uniquely by a function of $M_s = M_w/P$

$$J_e^0 \propto v' M_s / M_e \quad (16)$$

Considering that g_2 value is roughly equal to $(2/P)$ as is shown in Figure 8, $\log J_e^0$ vs. $\log 2M_w/P$ plots for multi-branched star polymers also deviate from the chain line, though we do not show the plots. These results seem to suggest that J_e^0 of multi-branched star polymers is affected by both the reduced flexibility of chain near central branch point and the expansion of chains, while η_0 mainly by the latter.

The result shown in Figure 7 indicates that the correction of molecular weight by g_2 is excess. As reported in the previous paper,²⁴ when the molecular weight of a branch M_s is near 55,000, J_e^0 is independent of the molecular weight at $P < 7$, while it increases in proportion to the molecular weight at $P \geq 7$. Considering these facts, it is anticipated that if we correct the molecular weight by g_2 -value independent of the number of branches, g_2^* , the plot of J_e^0 against $g_2^* M_w$ would coincide well with the prediction of the extended Rouse theory. As an attempt, we assume that the real branching factor for multi-branched star polystyrenes, $g_2^* = g_2$ for $P \leq 6$ and $g_2^* = g_2$ at $P = 7$ for $P \geq 7$. This assumption is expressed by a broken line in Figure 8 as g_2^* . Using these values of g_2^* , J_e^0 for multi-branched star polystyrenes (closed marks) can fairly well be reduced as shown in Figure 7, except for multi-branched polymers having M_s lower than the critical molecular weight for entanglement,^{1,2} $M_c = 38,000$, whose data are indicated by closed square with parenthesis. Though the reason why the g_2^* is constant for $P \geq 7$ is not yet clear enough, it might be attributed to the extra extension of chains due to the non-Gaussian distribution of the segments and the core formation by the less flexible chains at the center of the multi-branched star molecules.

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