

Characterization and Rheological Properties of Multi-Branched Star Polystyrenes[†]

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ABSTRACT: The star polymer samples were prepared by coupling narrow-distribution polystyryl anions with divinylbenzene and were characterized in terms of molecular weight, molecular weight distribution and coupling ratio. Dynamic viscoelastic properties of star-shaped polystyrenes having different molecular weights ($M_s = 1.3 \sim 20 \times 10^4$) and numbers ($P = 7 \sim 39$) of branches have been measured. The zero-shear viscosity η_0 depends strongly upon the molecular weight at constant P , while it depends much less at constant M_s . Molecular weight dependence of the steady-state compliance J_e° are quite complicated. J_e° increases with increasing molecular weight at constant P . When M_s is constant, J_e° is independent of molecular weight at $P \leq 7$ and increases at $P \geq 7$. Values of J_e° are higher than those for the corresponding linear polymers. Relaxation spectra for star-shaped polystyrenes having many ($P \geq 15$) branches exhibit a two-step change on the long-time side. These two sets of relaxation times are attributed to the relaxation mechanism associated with ordinary intermolecular entanglements and to that peculiar to branched polymers. The difference in the entanglement compliance J_{eN}° for branched and linear polymers is smaller than that in J_e° .

KEY WORDS Polystyrene / Branched Polymer / Characterization / Viscoelasticity / Viscosity / Steady-State Compliance / Relaxation Spectrum / Entanglement / Molecular Weight Dependence /

Effects of temperature, molecular weight and concentration on the rheological properties of six-branched star polymers^{1,2} and star-shaped polystyrene mixtures³⁻⁵ were discussed in our previous papers. These studies have provided new information on the effect of branching on the rheological properties especially in the terminal and rubbery zones. Studies on multi-branched star polystyrenes having different numbers and lengths of branches must afford more extensive and valuable information for the effect of number and length of branches on the rheological properties of branched polymers, which

has never been obtained by similar studies with branched polymers having six or less branches. Here the "multi-branched" polymer means that having more than six branches. Multi-branched polymers prepared using divinylbenzene (DVB) as the coupling agent have unperturbed dimensions larger than those calculated with the random-flight assumption,^{6,7} because such a polymer has a microgel nodule in its center.^{6,8-12} The non-Gaussian distribution of the chain segments near the center of molecule affects on the properties related to the spatial extensions, such as intrinsic viscosity, zero-shear viscosity, steady-state compliance and so on.

In this paper, the viscoelastic properties of multi-branched star polystyrenes prepared by

[†] Rheological Properties of Anionic Polystyrenes XI.

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use of DVB as the coupling agent have been measured over a wide range of frequency and temperature, comparing results with those for the corresponding linear and star-shaped polystyrenes having the number of branches of six and/or less. Prior to the viscoelastic measurements, the dilute solution properties of the multi-branched star polystyrenes have been measured and the characterization with respect to some molecular parameters has been made.

EXPERIMENTAL

Materials

The polystyryl anions used in the coupling reaction were prepared in benzene-tetrahydrofuran using *n*-butyllithium as an initiator. The parent polymer was obtained by terminating and purifying a part of the polystyryl anion with methanol. The polymerization procedure was similar to that described before.^{1,3} A very small amount of divinylbenzene (DVB) was used as the coupling agent. The concentration of DVB was 3.44×10^{-3} mol ml⁻¹ in benzene. It was found that each star-shaped polymer thus prepared had a rather sharp molecular weight distribution, which was measured by means of the gel permeation chromatograph. The quantity of residual parent polymers in the product was below a few percent.^{6,12} However, the polymer was fractionated by precipitation in benzene-methanol systems to remove higher and lower molecular weight fractions present in small amounts. The samples thus prepared were dried in a vacuum oven at 60°C.

It was reported by several authors⁸⁻¹⁰ that the copolymerization reaction of polystyryl anion and *para*-DVB can conveniently be separated into three steps. First, each living polystyrene initiates polymerization to produce linear poly(*p*-DVB) chains having a degree of polymerization $DP = k$, where k is the mole ratio of DVB to polystyryl anion, because the reactivity of divinylbenzene with

organo-lithium compounds is ten times higher than that of residual double bonds produced by coupling.^{6,9} In the next step, pendant double bonds may be crosslinked, and each crosslinking necessarily includes one polystyrene branch. In the final step, intramolecular ring formation is favoured, resulting in small densely crosslinked nuclei of DVB with a limited number of branches. Accordingly, products prepared by the anionic copolymerization of styrene and DVB are star-shaped polymers which are of more or less extended nuclei, *i.e.*, small particles. Thus, the number of branches is calculated by the following equation:¹⁰

$$P' = \frac{m_b \cdot M_n(\text{star})}{M_n(\text{branch})} \quad (1)$$

where m_b is the weight fraction of styrene in styrene-DVB system, and M_n is the number-average molecular weights.

In Table I the number- and weight-average molecular weights, molecular weight distribution for the star and parent polystyrenes, intrinsic viscosities of the star polymers, and coupling ratios P are shown. M_n (OS) and M_w (LS) in this table are respectively the number and weight-average molecular weights determined by the osmotic pressure and light-scattering methods. On the other hand, M_w/M_n (GPC) in the fourth column of this table was calculated from gel permeation chromatograph (GPC). M_w in the fifth column is the product of M_w/M_n (GPC) and M_n (OS). M_w calculated from M_w/M_n (GPC) agree fairly well with M_w determined by the light-scattering method.^{1,3} The coupling ratio P was calculated as the ratio of M_n of a star polymer to that of the parent one, and is equal to the ratio $M_n(\text{star})/M_n(\text{branch})$ in eq 1. The P values in this table are not exactly equal to but different by a factor m_b from the number of branches P' . The weight fraction of styrene in the styrene-DVB system, m_b , was varied from 0.94 to 0.98 in this study. Nevertheless, we used P as a measure of the number of branches because of $m_b \approx 1$.

Rheological Properties of Star Polystyrenes

Table I. The number- and weight-average molecular weights and molecular weight distribution for star and parent polystyrenes, intrinsic viscosity of star polymers, coupling ratio P , and molar ratio of DVB to polystyryl anion k

Sample	$M_n \times 10^{-4}$ (OS)	$M_w \times 10^{-4}$ (LS)	M_w/M_n (GPC)	$M_w \times 10^{-4}$	$[\eta]^a$	Parent polymer			k	P
						$M_n^b \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n		
LM1	220	—	1.19	262	0.279	5.68	6.21	1.09	30	38.7
LM2	193	243	1.21	234	0.269	6.01	6.55	1.09	20	32.1
LM3	73.6	—	1.17	86.1	0.282	5.02	5.48	1.09	7	14.7
LM4	124	127	1.19	148	0.280	5.62	6.12	1.09	10	22.1
LM5	156	200	1.21	189	0.274	5.25	5.72	1.09	13	29.7
LM6	80.4	—	1.19	95.7	0.320	6.23	6.85	1.10	5.5	12.9
LM7	34.3	—	1.30	44.6	0.276	4.8 ^c	—	—	—	7.2 ^d
LM8	22.3	29.6	1.18	26.3	0.139	1.17	1.27	1.08	8	19.1
LM9	79.1	85.8	1.20	94.9	0.225	3.43	3.73	1.09	8	23.1
LM10	124	136	1.16	144	0.345	8.21	9.11	1.11	8	15.1
LM11	160	—	1.18	189	0.404	11.3	12.5	1.11	8	14.2
LM12	267	—	1.13	302	0.474	17.9	20.1	1.12	8	14.9

^a Measured in cyclohexane at 34.5°C.

^b Identical to M_s .

^c Calculated as M_n (star)/ P .

^d Estimated by the interpolation of $[\eta]$ vs. P plots from Figure 1.

As is seen from Table I, LM1~7 have almost constant molecular weight of branches (M_s) of near 55,000, and LM3, 6, 10, 11, and 12 have almost constant number of branches P of near 15, and LM4, 8, and 9 have constant P of near 20. All the undiluted samples of LM series shown in Table I were used to investigate the molecular weight dependence of rheological properties.

Worsfold *et al.*⁸ reported that the number of branches for star polymers synthesized by copolymerization of styrene and DVB was a function of the overall concentration, of the amount of DVB, and of the molecular weight of the linear precursor. The overall concentration used in this study is not always constant but does not differ largely for each run. Therefore, it is instructive to see qualitatively the relation between the molar ratio of DVB to polystyryl anion, k , and the number of branches, P , in a molecule. The values of k and P are shown in Table I as well as the number-average molecular weight of parent polystyrenes, *i.e.*, molecular weight of a

branch, M_s . As is evident from this table, when M_s is below about 6×10^4 and P is below 30, P of star polymers obtained is a little higher than $2k$. When k is constant, the number of branches increases with decreasing molecular weight of parent polymers; for instance, LM9 with shorter branches has P of about $3k$, but other samples having longer branches have P lower than $2k$. This suggests that the number of branches is highly controlled by a pronounced diffusion of the reaction.¹⁰ However, even if the amount of DVB increases, the number of branches is apt to level off at $k > 20$. This may imply that the coupling reaction becomes more and more hindered as polystyrene chains increase, because the primary chains should move through a shield of polystyrene branches before crosslinking can take place.¹⁰

Measurement of Viscoelasticity

The measurements of the rheological properties of the star polymers were carried out with a concentric cylinder type rheometer de-

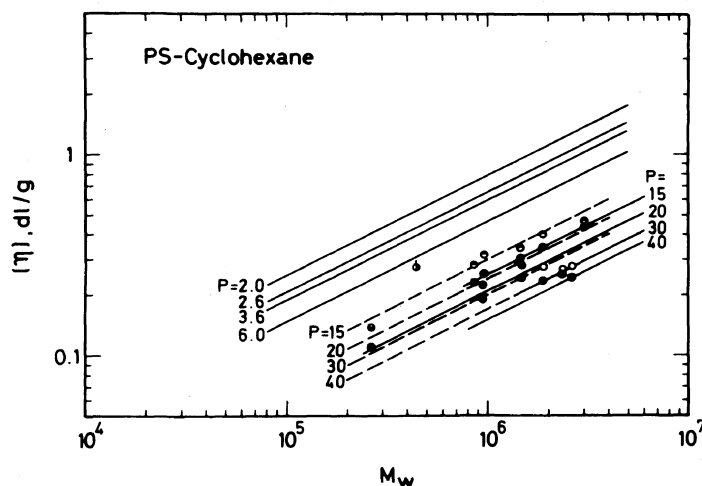


Figure 1. The relation between $[\eta]$ and M_w for multi-branched star polystyrenes. P indicates number of branches. Closed circles indicate results calculated from eq 8 and the other circles, experimental values measured at 34.5°C.

scribed in the previous papers.¹⁻⁵ This rheometer enables us to measure the storage shear modulus G' and loss modulus G'' as functions of the angular frequency ω at different temperatures. The measuring frequency ranged from 4×10^{-3} to 0.5 CPS and the temperature from 120 to 22°C.

The frequency dependence curves of the viscoelastic functions at various temperatures were superposed into their respective master curves according to the time-temperature superposition principle.

RESULTS AND DISCUSSION

Characterization of Star-Shaped Polystyrenes

In Figure 1, intrinsic viscosities $[\eta]$ in cyclohexane at 34.5°C shown in Table I are plotted against M_w for star-shaped polystyrenes used in this study (open, upper and lower black circles) together with results reported previously.^{1,3,4} P in this figure indicates the number of branches. The uppermost straight line indicated by $P=2$ corresponds to the viscosity equation proposed previously, for narrow-distribution polystyrenes.¹

$$[\eta]_1 = 7.9 \times 10^{-4} M_w^{0.5} \quad (2)$$

The straight lines indicated by $P=2.6, 3.6,$ and 6 represent results obtained for star polymers having average number of branches $P=2.6, 3.6,$ and $6,$ respectively. All the lines have the slope of 0.5 as reported previously.^{1,3,4} As is seen from this figure, $[\eta]$ at the same molecular weight decreases with increasing number of branches. The right-black circle with pip in this figure is for LM7. The value of $P (=7.2)$ in Table I was estimated by interpolation in this figure.

$[\eta]_b$ for samples having P near 15 (●) and 20 (⊖) can also be represented by straight lines having the slope of 0.5, as is indicated by the broken line. Moreover, if we assume that $[\eta]_b$ for star polymers having P of near 30 and 40 may be represented by straight lines having an identical slope, the broken lines indicated by $P=30$ and 40 in Figure 1 can be obtained.

$$[\eta]_b = 3.0 \times 10^{-4} M_w^{0.5} \quad \text{for } P=15 \quad (3)$$

$$[\eta]_b = 2.4 \times 10^{-4} M_w^{0.5} \quad \text{for } P=20 \quad (4)$$

$$[\eta]_b = 2.0 \times 10^{-4} M_w^{0.5} \quad \text{for } P=30 \quad (5)$$

$$[\eta]_b = 1.7 \times 10^{-4} M_w^{0.5} \quad \text{for } P=40 \quad (6)$$

Several authors^{6,7,13-23} have experimentally

and theoretically shown that θ_{A_2} for the branched polymers is lower than that for the linear ones. Here, θ_{A_2} is the temperature at which the second virial coefficient $A_2=0$. Moreover, the more and shorter branches a polymer has, the lower θ_{A_2} becomes. Therefore, $[\eta]$ for multi-branched star polymers in cyclohexane at constant temperature (34.5°C) are not obtained under the same thermodynamic conditions. However, Candau and coworkers²² suggested that θ_{A_2} should be higher than θ_α at which the expansion factor $\alpha=1$, though the difference between θ_{A_2} and θ_α is small for star polymers. This shows that chains of star polymers are already slightly expanded when A_2 is zero. Moreover, it is noteworthy that as temperature increases beyond θ_{A_2} , branched polymers expand less rapidly than linear ones do.^{7,12,13,16-24} It was also reported¹⁴ that $[\eta]$ measured at θ_{A_2} for four- and six-branched polystyrenes differed from $[\eta]$ measured at 35°C by not more than experimental errors.

Zilliox⁷ has published intrinsic viscosity data on a series of highly branched star polystyrenes. The average number of branches ranges from 6 to 15.5. He measured the intrinsic viscosity in cyclohexane at temperature θ_{A_2} and proposed experimental equations of $[\eta]_b$ for star polymers with P higher than ten;

$$[\eta]_{*,\theta} = 1.18[\eta]_{s,\theta} + 3 \quad (7)$$

or

$$[\eta]_{*,\theta} = 1.25[\eta]_{s,\theta} \quad (8)$$

where $[\eta]_{*,\theta}$ and $[\eta]_{s,\theta}$ indicate intrinsic viscosities at θ_{A_2} for multi-branched and parent polymers, respectively. $[\eta]_{s,\theta}$ can be calculated from eq 2, using M_w for parent polymers. Therefore, if eq 7 or 8 can be also applied to star polymers having P higher than 15.5, intrinsic viscosities at θ_{A_2} can be obtained for star polymers with more branches.

The closed circles in Figure 1 represent results estimated from eq 8, which may be

more appropriate than eq 7 because the former passes the origin and $[\eta]_{*,\theta}$ becomes zero when $[\eta]_{s,\theta}$ is zero. As is seen from this figure, $[\eta]_{*,\theta}$ for all the star polymers are lower than $[\eta]_b$ measured at 34.5°C. This result suggests that θ_{A_2} for multi-branched polymers is lower than 34.5°C, which is θ_{A_2} for linear polystyrenes. If we assume that $[\eta]_{*,\theta}$ for multi-branched polymers can be represented by straight lines with the slope of 0.5, the solid straight lines indicated by $P=15, 20, 30,$ and 40 may also be obtained in the same manner as $[\eta]_b$ (broken lines) at 34.5°C.

$$[\eta]_{*,\theta} = 2.5 \times 10^{-4} M_w \quad \text{for } P=15 \quad (9)$$

$$[\eta]_{*,\theta} = 2.1 \times 10^{-4} M_w \quad \text{for } P=20 \quad (10)$$

$$[\eta]_{*,\theta} = 1.7 \times 10^{-4} M_w \quad \text{for } P=30 \quad (11)$$

$$[\eta]_{*,\theta} = 1.5 \times 10^{-4} M_w \quad \text{for } P=40 \quad (12)$$

The relation between $[\eta]$ and M_w for star polymers having constant molecular weight of branches M_s of 55,000 is shown in Figure 2, where the linear polymer is considered to be a two-branched star polymer. Values for star polymers having P lower than six (\odot) are estimated by interpolation of the molecular weight dependence of $[\eta]$ shown in Figure 1. Open circles indicate data measured at 34.5°C for star polymers mentioned above. As is shown in Figure 2, plots of $[\eta]_b$ for the star polymers and linear polymer of $M_w=110,000$ mount well on a horizontal broken line.

From the definition that $g_\eta^3 = [\eta]_b / [\eta]_1$,

$$[\eta]_b = \left(\frac{P}{2}\right)^{1/2} g_\eta^3 [\eta]_{\text{span}} \quad (13)$$

where $[\eta]_1$ is the intrinsic viscosity for a linear polymer having the same molecular weight as that of the star polymer and $[\eta]_{\text{span}}$ is the intrinsic viscosity for a linear polymer having two branches of the same length as that of the star polymer. When we know the relation between g_s and g_η , $[\eta]_b$ can be calculated from eq 13, using g_s^2 given by the following equation²⁵

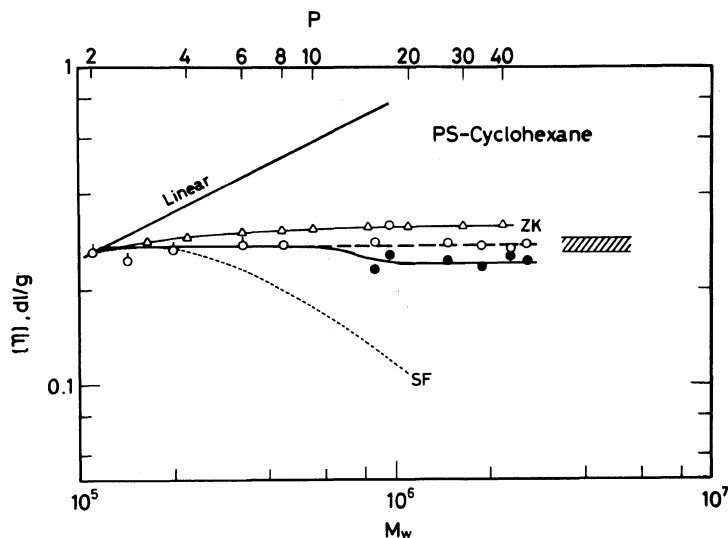


Figure 2. The relation between $[\eta]$ and M_w for star polymers having constant molecular weight of branches, near 55,000. Triangles indicate values estimated from g_s^2 calculated from eq 14 and ZK relation ($g_s = g_n^3$), open circles, experimental values at 34.5°C, and closed circles, values calculated from eq 8. The hatched portion represents a range of intrinsic viscosities obtained by using eq 14 and the relation of $g_s = g_n^{2.5}$ for star polymers having P lower than 40.

$$g_s^2 = (3P - 2)/P^2 \quad (14)$$

Here, g_s^2 is the ratio of the mean-square radius of gyration $\langle s^2 \rangle_b$ for a star polymer to that for the corresponding linear polymer having the same molecular weight. Triangles in Figure 2 represent values estimated from the g_s^2 calculated from eq 14, and the Zimm-Kilb (ZK) relation²⁶ ($g_s = g_n^3$). Calculated values (Δ) increase gradually with increasing number of branches and are higher than experimental values (\circ). However, if we use an experimental relation $g_s = g_n^{2.5}$, which can be applied to star polymers with P below six^{1,6,14,27} instead of the ZK relation, calculated values of the intrinsic viscosity range from 0.26 to 0.29 dl g^{-1} for star polymers having P lower than 40, and they agree well with experimental values, as is indicated by the hatched portion. Quack *et al.*²⁸ reported similar results for star-shaped polyisoprenes linked by DVB, although intrinsic viscosities for four- and six-branched polymers are higher than $[\eta]_{\text{span}}$ for a linear polymer^{12,14} suggesting that $[\eta]_b$ has a

maximum at P of near six.²⁹

When we choose $[\eta]_{*,\theta}$ as an intrinsic viscosity at the real θ temperature for multi-branched polymers with a constant molecular weight of branches (\bullet), the intrinsic viscosity for multi-branched polymers is initially constant and then decreases, approaching a constant value at P of near 15 with increasing number of branches. Similar results were reported by Zilliox⁷ for star polystyrenes with P lower than 15.5. He measured the intrinsic viscosity with cyclohexane at temperature θ_{A2} , as mentioned before. These results agree qualitatively with theoretical prediction given by Stockmayer and Fixman³⁰;

$$[\eta]_b = 2^{-1/2} P^2 [2 - P + 2^{1/2}(P - 1)]^{-3} [\eta]_{\text{span}} \quad (15)$$

although the discrepancy becomes large with increasing branch number, because their theory predicts that $[\eta]_b$ is initially constant and then decreases with increasing P , as shown by the dotted curve (SF). The constant value of $[\eta]_b$ obtained in this study is 0.24 dl g^{-1} , which is calculated from eq 2 and 8.

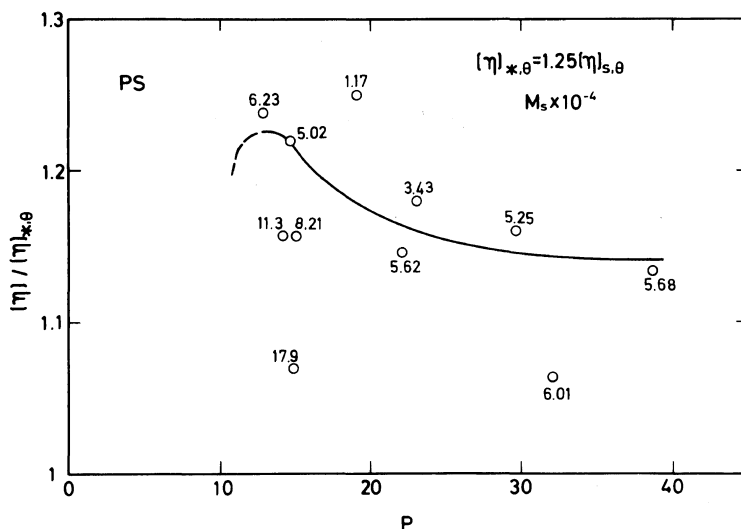


Figure 3. The relation between ratio $[\eta]/[\eta]_{*,\theta}$ and P for multi-branched polystyrenes.

These results imply that the ZK relation ($g_s = g_n^3$) and the experimental relation ($g_s = g_n^{2.5}$) do not hold, and that an exponent of the relation between g_s and g_n may be lower than 2.5 or that g_s^2 can not be calculated from eq 14 for multi-branched star polymers under θ condition.

Figure 3 shows the relation between the ratio $[\eta]/[\eta]_{*,\theta}$ and P for multi-branched polystyrene, where $[\eta]$ and $[\eta]_{*,\theta}$ are experimental values measured at 34.5°C and calculated ones estimated from eq 8, respectively. Numbers in this figure represent the molecular weight of branches M_s . We may consider that $[\eta]/[\eta]_{*,\theta}$ is a measure of deviations of θ_{A2} for branched polymers from the value for linear polymers (θ). As is seen in Figure 3, $[\eta]/[\eta]_{*,\theta}$ for star polymers with constant number of branches of near 15 and 20 decreases with increasing M_s , suggesting that $\theta - \theta_{A2}$ becomes larger as branches become shorter. Roovers *et al.*¹⁴ reported that $[\eta]$ measured at 35°C agreed fairly well with $[\eta]$ measured at θ_{A2} for four- and six-branched polymers to suggest that $[\eta]/[\eta]_{*,\theta}$ is unity for star polymers with P lower than six. From these results reported by Roovers *et al.*¹⁴ and those obtained in this study, $[\eta]/[\eta]_{*,\theta}$ for star polymers with constant M_s may have a

maximum at P of near 15. This may imply that $\theta - \theta_{A2}$ for star polymers with constant M_s also has a maximum at P of near 15. It is known^{6,7} for star polymers having P lower than 15 that $\theta - \theta_{A2}$ becomes larger as the number of branches increases, but few studies on the dilute solution properties for star polymers with many branches have been carried out. Therefore, it is necessary to examine experimentally whether $\theta - \theta_{A2}$ for star polymers with constant M_s has a maximum or not.

We know that an experimental relation between g_s^2 and P cannot directly be estimated by eq 14, because samples used generally have more or less broad molecular-weight distribution. Furthermore, multi-branched star polymers have more or less extended nucleus, and consequently g_s^2 for multi-branched polymers should be estimated by not only the number of branches but also g_s^2 for the branched nucleus, as reported by Burchard.³¹ In practice, experimental values of g_s^2 for star-shaped polystyrenes at θ_{A2} agree well with theoretical ones up to about nine branches.⁶ For polymers with more branches, however, experimental values of g_s^2 become higher than theoretical ones, suggesting that molecules have greater $\langle s^2 \rangle$ at the temperature at which

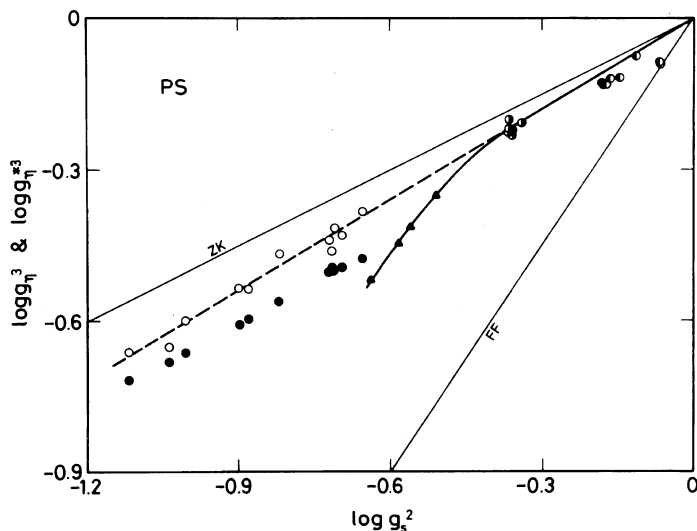


Figure 4. The relation between g_s^3 and g_s^2 for star-branched polystyrenes. Open circles indicate data evaluated from $[\eta]_b$ at 34.5°C for multi-branched polymers with P above six, left black circles for mixtures of star polymers having P near 2.6 and 3.6 and right black circles for six-branched polystyrenes. Closed circles represent data evaluated from $[\eta]_{*,\theta}$, instead of $[\eta]_b$. Triangles indicate results reported by Zilliox.⁷

A_2 becomes zero.^{6,7} Experimental values of g_s^2 for comb-shaped polystyrenes show tendency to decrease with increasing number of branches, and to level off at high densities of branching.²⁰ These results suggest that g_s^2 calculated by eq 14 for multi-branched star polymers having many branches is lower than experimental one, though no experimental test for star polystyrenes of P above 16 has been reported yet.

The relation between $g_n^3 = [\eta]_b / [\eta]_1$ and g_s^2 for star polystyrenes is shown in Figure 4, where g_n^3 was calculated from the molecular weight and $[\eta]_b$ at 34.5°C given in Table I using eq 2, and g_s^2 from P in Table I using eq 14. In this figure, open circles indicated data for star polymers having P above 6, left black circles, those for star polymers³ having P of near 2.6 and 3.6, and right black circles, those for star polymers having P of near 6. Triangles represent results at θ_{A2} for star polymers having P from 8.7 to 15.5 reported by Zilliox.⁷ ZK and FF curves represent the relation $g_s = g_n^3$ and $g_s = g_n$, respectively. The ZK relation was presented by Zimm and Kilb²⁶ for star-shaped

polymers, and the FF relation is the well-known Fox–Flory relation for linear polymers. The middle straight line in this figure has a slope of 0.6 to give a relation, $g_s = g_n^{2.5}$. Similar results were reported for star-shaped polymers having P lower than 6.^{1,6,13,14} However, for polystyrenes having more branches at θ_{A2} (\blacktriangle), the slope increases,^{6,7} suggesting that $g_s = g_n^{1.85}$. Such a difference may be due to the fact that g_s^2 calculated from eq 14 for multi-branched polymers is somewhat lower than experimental ones,^{6,7} and that intrinsic viscosity measurements were carried out at other temperature (34.5°C) than θ_{A2} to give somewhat higher $[\eta]$.

Closed circles in Figure 4 indicate values of $g_n^{*3} = [\eta]_{*,\theta} / [\eta]_1$ obtained by the use of $[\eta]_{*,\theta}$ calculated from eq 8 instead of $[\eta]_b$ at 34.5°C, and g_s^2 calculated from eq 14. Here again, calculated values (\bullet) are higher than experimental ones (\blacktriangle). The method to evaluate the true values of g_s^2 for multi-branched star polymers will be proposed in the succeeding paper.³²

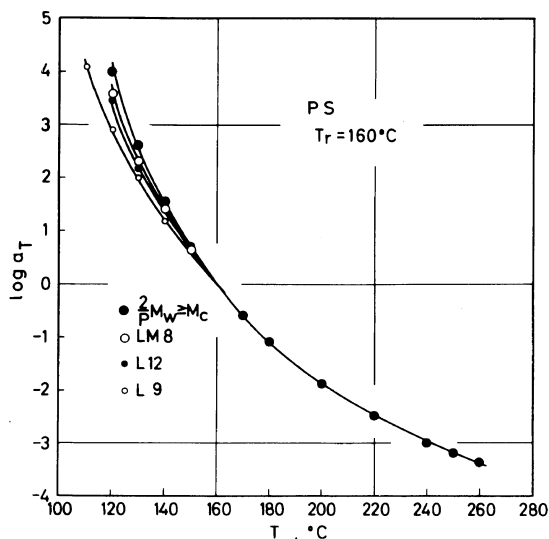


Figure 5. The logarithm of the shift factor a_T plotted against temperature for star and linear polystyrenes. Large closed circles represent the result for $(2/P)M_w \geq M_c$, large open circles for $(2/P)M_w = 27,500$ (LM8), small closed circles for $(2/P)M_w = 14,800$ (L12),³³ and small open circles for $(2/P)M_w = 8,900$ (L9).

Temperature Dependence of Viscoelasticity

The time-temperature superposition was applied to frequency dependence curves of storage shear modulus G' and loss modulus G'' measured at different temperatures, and the shift factor a_T was determined in the process of superposition.

The shift factor a_T for star-shaped polystyrene samples used in this study is plotted against temperature T in Figure 5 as well as that for narrow-distribution linear polystyrenes reported previously.³³ In this figure, large closed circles indicate data for star and linear polymers having the span molecular weight $(2/P)M_w$ higher than M_c (M_c is the critical molecular weight near 38,000 for linear polystyrenes.³³⁻³⁵) large open circles, for star polystyrene LM8 [$(2/P)M_w = 27,500$], small closed circles, for linear polymer L12 ($M_w = 14,800$), and small open circles, for linear polymer L9 ($M_w = 8,900$). The values for linear polymers have been discussed in detail by Onogi *et al.*³³ The shift factor a_T for polymers whose $(2/P)M_w$ is higher than M_c is independent of the molecular weight and number

of branches. Similar results were reported by Fujimoto *et al.* for comb-shaped polystyrenes^{36,37} and by Graessley and coworker for four- and six-branched star polystyrenes.³⁸ However, the shift factor a_T for samples having $(2/P)M_w$ lower than M_c becomes low.

As is well-known, if the shift factor a_T can be expressed by a WLF type equation, the plot $-(T - T_r)/\log a_T$ against $(T - T_r)$ should give a straight line, where T_r is the reference temperature. From the slope and intercept of such a plot, the free volume parameters such as the Vogel temperature T_0 and temperature coefficient of the fractional free volume α_f can be evaluated.³⁵ The plot for the above linear and star polymers is given in Figure 6. The symbols are the same as in Figure 5. The evaluated values of free volume parameters are tabulated in Table II, where f_{160} and f_g are the fractional free volumes at 160°C and glass transition temperature, $T_g = 100^\circ\text{C}$, respectively.

It is evident from Table II that T_0 for linear polymers having $(2/P)M_w$ ($=M_{\text{span}}$) lower than M_c decreases with decreasing the molecular weight, while α_f remains almost con-

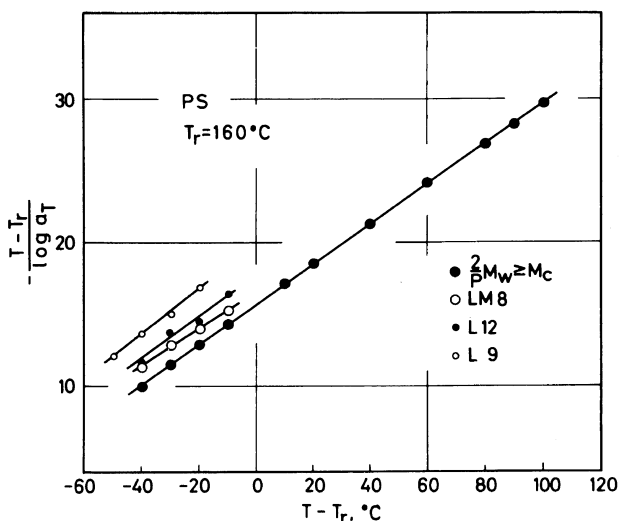


Figure 6. Linear plots of $-(T-T_r) \log a_T$ vs. $T-T_r$ for star and linear polystyrenes. The reference temperature is 160°C .

Table II. Free volume parameters evaluated from the temperature dependence of the shift factor

	Sample	$M_{\text{span}} = (2/P)M_w$	$\frac{\alpha_f}{\text{deg}^{-1}}$	$\frac{T_0}{^\circ\text{C}}$	f_{160}	f_g
Star	High M_w	$\geq M_c$	5.42×10^{-4}	47.9	0.0608	
	LM8	27,500	4.29×10^{-4}	30.4	0.0556	
Linear	High M_w	$\geq M_c$	5.42×10^{-4}	47.9	0.0608	0.0283
	L12	14,800	5.20×10^{-4}	38.1	0.0634	$T_g = 100^\circ\text{C}$
	L9	8,900	5.28×10^{-4}	31.8	0.0677	

stant.³³ On the other hand, for star polymers whose M_{span} is lower than M_c , both of T_0 and α_f are lower than those for higher molecular weight samples. The numerical values for the free-volume parameters shown in this table tell us that linear polystyrenes having M_w below M_c possess more free volume as compared with those having M_w above M_c at the same temperature,³³ while the reverse is the case for star polystyrenes at temperatures above 115°C . For example, $f_{160} = 0.0608$ for linear and star polystyrenes having $M_{\text{span}} > M_c$, while $f_{160} = 0.0677$ for linear polymer L9 having $M_w = 8,900 < M_c$, and $f_{160} = 0.0556$ for star polymer LM8 having $M_{\text{span}} = 27,500 < M_c$. The

reference temperature T_r' chosen for LM8 is 172°C , at which this polymer has the same fractional free volume as that for polymers having M_{span} higher than M_c at 160°C , namely, 0.0608. This lack of free volume in LM8 causes the shift of G' and G'' curves for this polymer to the low-frequency side in the transition zone. This abnormal behavior was observed also for 50 wt% solutions of six-branched polystyrenes.¹

Frequency Dependence of Viscoelastic Functions

Figures 7 and 8 show respectively master curves of G' and G'' for star-shaped polysty-

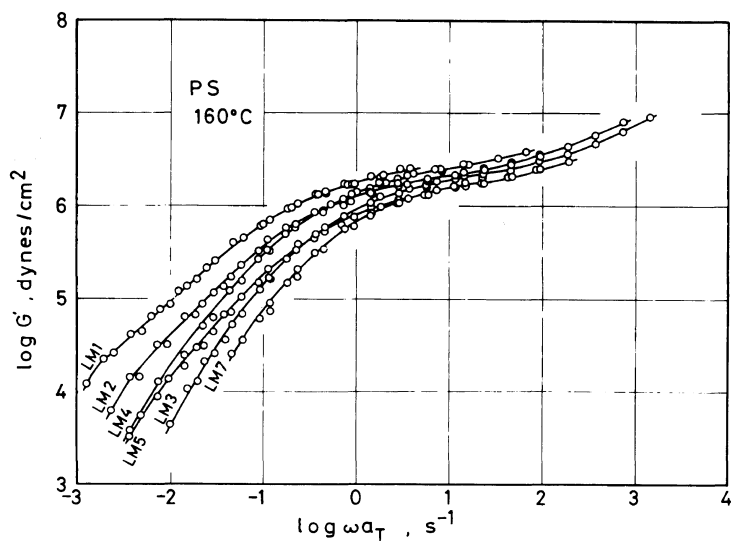


Figure 7. Master curves of G' for multi-branched polystyrenes having M_s of near 55,000. The reference temperature is 160°C.

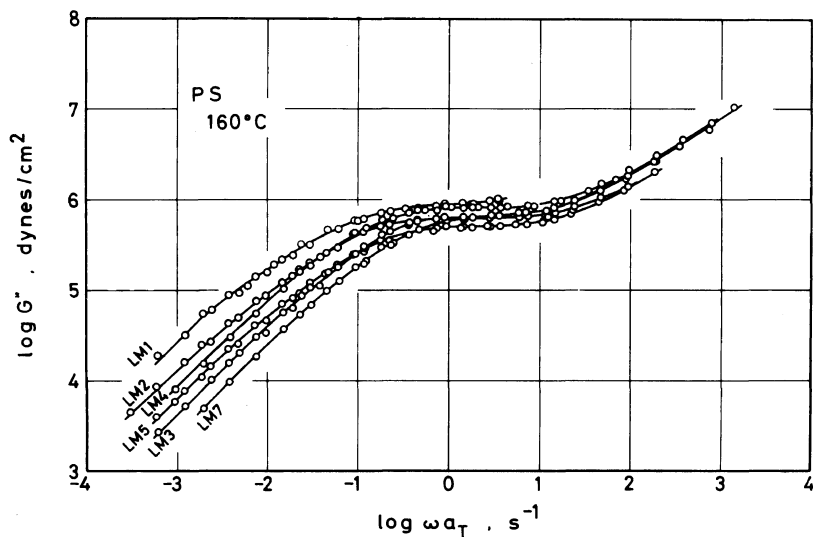


Figure 8. Master curves of G'' for multi-branched polystyrenes having M_s of near 55,000. The reference temperature is 160°C.

renes having a constant length ($M_s \approx 55,000$) but different numbers of branches at 160°C. The number of branches ranges from 7.2 (LM7) to 38.7 (LM1). As can be seen from these figures, G' and G'' curves in the terminal zone shift to the low frequency side as molecular weight increases, but the shift is rather small. For example, although the ratio of

molecular weight of LM1 having the highest molecular weight to that of LM7 having the lowest molecular weight is about 6, as can be seen from Table I, the ratio of frequencies at which G' of these samples has a value of 10^4 dyn cm $^{-2}$ is estimated as only 25.

In Figures 9 and 10 master curves of G' and G'' for star polystyrenes having nearly equal

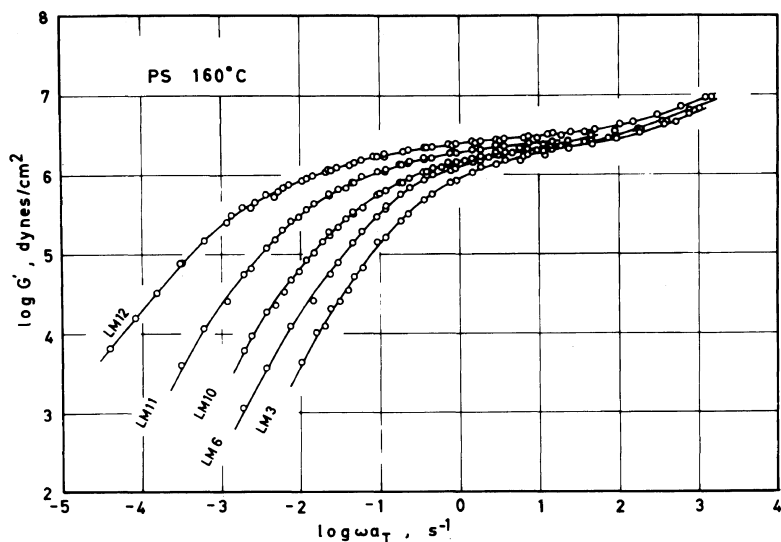


Figure 9. Master curves of G' for multi-branched polystyrenes having P of near 15. The reference temperature is 160°C .

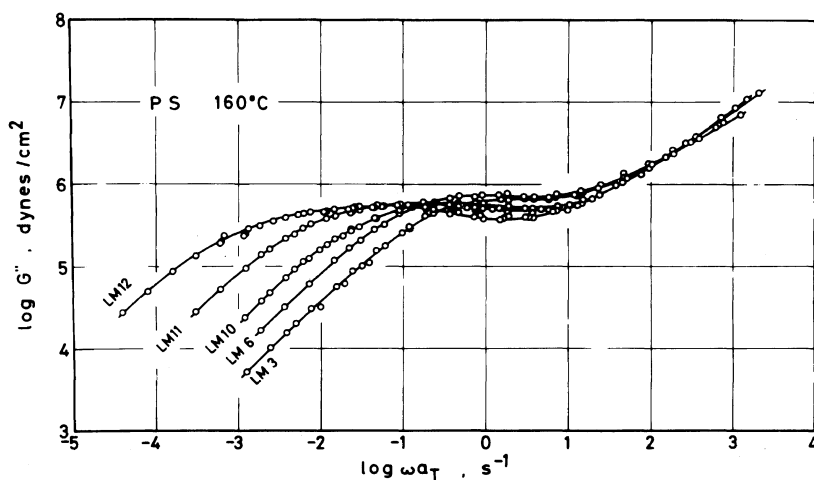


Figure 10. Master curves of G'' for multi-branched polystyrenes having P of near 15. The reference temperature is 160°C .

numbers ($P \approx 15$) but different lengths of branches at 160°C are shown, respectively. These master curves in the terminal zone shift to the low frequency side much more than those for star polymers having a constant length of branches shown in Figures 7 and 8. For example, the ratio of frequencies, at which G' for LM8 having the lowest molecu-

lar weight and LM12 having the highest molecular weight has a value of 10^4 dyn cm^{-2} is about 270, though the ratio of molecular weights of these samples is only about 3.5, as can be seen from Table I.

Similar behavior of G' and G'' can be observed also for star polymers having about 20 branches, whose master curves are shown in

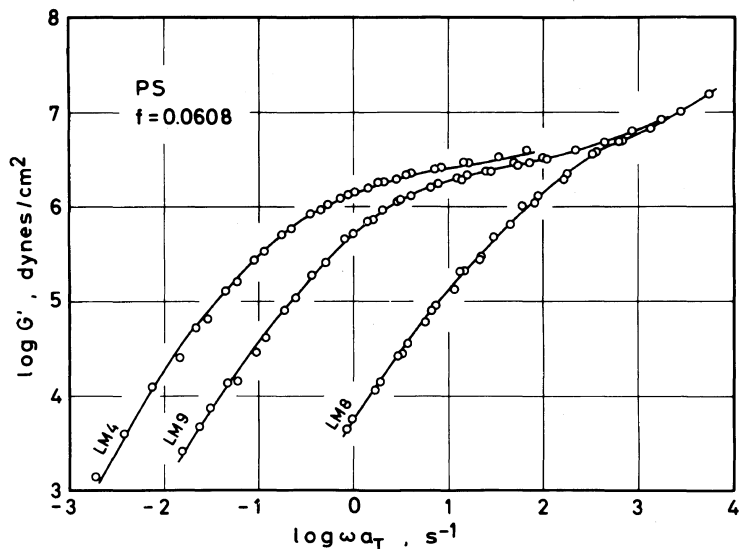


Figure 11. Master curves of G' for multi-branched polystyrenes having P of near 20 in the iso-free-volume state, $f=0.0608$.

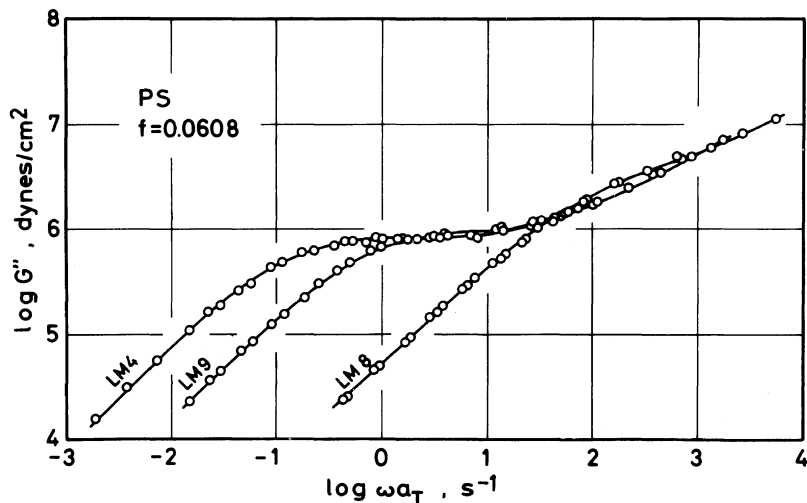


Figure 12. Master curves of G'' for multi-branched polystyrenes having P of near 20 in the iso-free-volume state, $f=0.0608$.

Figures 11 and 12. Master curves in these figures were obtained in the iso-free-volume state, where $f=0.0608$. Therefore, the reference temperature for LM8 ($M_s=11,700$), 172°C , is higher than that for LM4 ($M_s=56,200$) and LM9 ($M_s=34,300$) of 160°C . It is also noticed that the master curves for the above three samples unite with one another in

the transition zone, disregarding differences in the length of branches.

Relaxation Spectrum

As mentioned in the preceding section, the viscoelastic properties of star polymers vary very sensitively with the number and length of branches. In order to make the effect of the

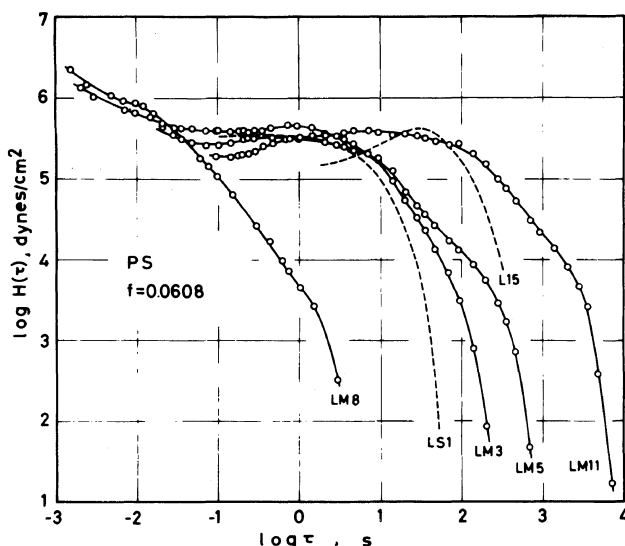


Figure 13. A comparison of relaxation spectra for narrow-distribution linear and star-branched polystyrenes.

number and length of branches clearer, relaxation spectra for some of the multi-branched star polystyrenes so far mentioned, a linear polystyrene, L15, and a six-branched star polymer, LS1, were determined from master curves of G' using Tshoegl's equation.³⁵ To facilitate comparison, all the spectra were determined in the iso-free-volume state and are shown in Figure 13. All the samples shown in this figure can be classified into the following five groups according to the number and length of branches:

(1) Samples having branches of almost constant M_s near 110,000 and different numbers

$$\text{L15} : P = 2, \quad M_s = 107,000$$

$$\text{LM11} : P = 14.2, \quad M_s = 113,000$$

(2) Samples having branches of almost constant M_s near 55,000 and different numbers

$$\text{LS1} : P = 6.1, \quad M_s = 58,900$$

$$\text{LM3} : P = 14.7, \quad M_s = 50,200$$

$$\text{LM5} : P = 29.7, \quad M_s = 52,500$$

(3) Samples having branches of almost con-

stant P near 14 and different lengths

$$\text{LM3} : P = 14.7, \quad M_s = 50,200$$

$$\text{LM11} : P = 14.2, \quad M_s = 113,000$$

(4) Samples having constant M_w near 1,890,000 and branches of different numbers and lengths

$$\text{LM11} : P = 14.2, \quad M_s = 113,000$$

$$\text{LM5} : P = 29.7, \quad M_s = 52,500$$

(5) Samples having branches whose M_s is lower than $M_e = 18,000$

$$\text{LM8} : P = 19.1, \quad M_s = 11,700$$

Spectra for all the samples shown in Figure 13 seem to coincide with one another in the transition zone. This suggests that the rheological properties in the transition zone are never affected by the length and number of branches in the iso-free-volume state.

As is evident from Figure 13, the spectrum for linear polymer L15 has a peak in the long-time region and then falls off rapidly with increasing relaxation time, while that for multi-branched star polystyrenes ($P > 15$) has

a shoulder or break on the long-time side. Among samples having branches of constant M_s near 110,000 (L15 and LM11), L15 ($P=2$) shows a clear peak in the rubber-flow transition region as mentioned above, while LM11 ($P=14.2$) shows a broad peak in the same region. Another difference is that the relaxation spectrum for LM11 falls off less rapidly in the rubber-flow transition region, indicating that the longest relaxation time is longer. Relaxation spectra for star polymers having branches of constant M_s near 55,000 (LS1, LM3, and LM5) show also a broad peak around $\log \tau = 0$, at which a linear polymer L37 ($P=2$, $M_n=113,000$) reported in a previous paper³³ has a peak.

The weight-average molecular weight of LS1, LM3 and LM5 is 426,000, 861,000 and 1,890,000, respectively, but their τ_m , the relaxation time at which $H(\tau) = 5 \times 10^2 \text{ dyn cm}^{-2}$, increases only by a factor of three. This behavior differs from the well-known result for linear polymers,^{34,35} of which the longest relaxation time τ_m is proportional to $M_w^{3.4}$. On the other hand, when we compare τ_m of LM3 and LM11 having almost the same number of branches ($P \simeq 14$), we notice that τ_m of the latter material is about 30 times longer than that of the former, indicating that τ_m is proportional to $M^{4.4}$. Thus, the longest relaxation time of star polymers increases more rapidly when the total molecular weight is increased by increasing the length of branches than when it is increased by increasing the number of branches of equal length. This is clear when one compares the longest relaxation times of LM11 and LM5 having almost equal molecular weights. τ_m of LM11 having fewer but longer branches is about ten times longer than that of LM5 having more but shorter branches.

As mentioned before, relaxation spectra of star polystyrenes having many branches show a shoulder or break at the long-time end. This implies existence of a new relaxation mechanism at very long times. This mechanism

seems to be different from that associated with intermolecular entanglements. Graessley and Roovers³⁸ reported that there are two sets of distribution of relaxation times for four- and six-branched star polystyrenes having branches long enough to cause the enhancement of viscosity. A similar result was reported also for comb-shaped polystyrenes.³⁹ Now, it is noteworthy that even the spectrum of LM8 having about 20 branches shows a shoulder at long times, disregarding that branches are too short to form entanglements between others ($M_s < M_e$). A similar result was reported by Fujimoto *et al.*³⁷ for comb-shaped polystyrene having branches of molecular weight of only 1.8×10^4 . They considered existence of two relaxation mechanisms; one is a mechanism associated with the entanglement between parent polymers, and the other is that associated with the entanglement between parent polymer and branches. Therefore, the mechanism discussed for four- and six-branched star polymers having long branches may be different from that observed for multi-branched polystyrenes having shorter branches.

Now, we will compare relaxation spectra of LS1, LM3 and LM5 having about 6, 15 and 30 branches of almost equal M_s around 55,000. The spectrum of LS1 shows no shoulder, while those of LM3 and LM5 exhibit a marked one. Of course, the terminal zone shifts to the long-time side as the number of branches (total molecular weight) increases.

It is well-known that relaxation spectra for most suspensions manifest the so-called second plateau, which arises from long-time relaxation in structure formed by dispersed particles.⁴⁰⁻⁴² According to Masuda *et al.*,^{43,44} however, relaxation spectra of polystyrene and its solutions containing polybutadiene particles exhibit the second plateau in the long-time region in spite of the isolation of particles in the material. They attributed the long-time relaxation mechanism corresponding to the second plateau to the movement of each particle as a whole. Multi-branched star

polystyrenes employed in this study contain particles formed at the center of molecules, though their size is much smaller than those of polybutadiene particles mentioned above. Therefore, the above-mentioned shoulder appeared at the long-time end of relaxation spectra of multi-branched polymers may correspond to the second plateau observed for filled polymers, though it is very faint.

Zero-Shear Viscosity

The zero-shear viscosity η_0 characteristic of the terminal zone is defined by the following equations:

$$\eta_0 = \lim_{\omega \rightarrow 0} G''/\omega \quad (16)$$

In Figure 14 the molecular weight (M_w) dependence of the zero-shear viscosity η_0 reduced to the iso-free-volume state in which $f=0.0608$ is shown for star-shaped polystyrenes. Open circles indicate star polymers having about 15 branches, squares, those having about 20 branches, and triangles, those having about 30 branches, and a hexagon, one having about 40 branches. L and LS represent linear (two-branched) and six-branched polystyrenes,¹ respectively. Finally, LB represents mixtures of three- and four-branched polymers,³ which have the average number of branches of 3.6. η_0 of linear polymers is represented by a straight line having the slope of 3.5. η_0 of six-branched polymers is also represented by a straight line having the same slope. η_0 of LM7 ($P=7.2$) locates a little lower than the line for $P=6$ as seen from this figure. η_0 of star polymers with about 15 branches is proportional to 3.5 powers of M_w at lower molecular weights but to higher powers at higher molecular weights. η_0 for star polymers with about 20 branches is represented by a straight line having the slope of 3.5 at higher molecular weights, but the slope decreases at lower molecular weights.

As is evident from this figure, η_0 for all the star polymers (η_b) is always lower than that of linear polymers (η_l) at the same molecular weight in the range of the molecular weight

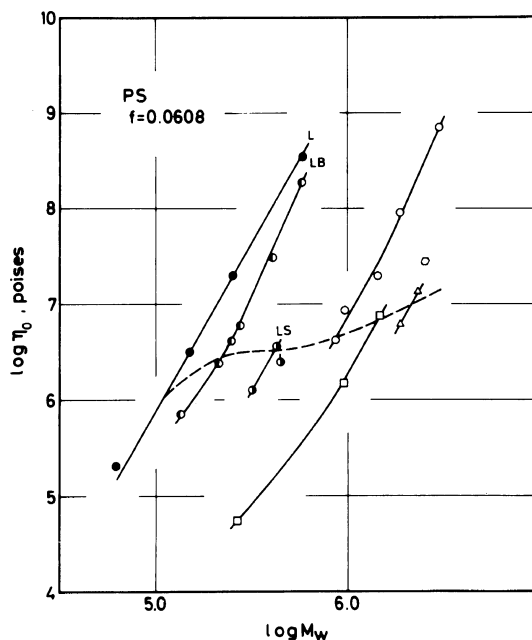


Figure 14. Molecular weight dependence of zero-shear viscosity η_0 for star polystyrenes reduced to the iso-free-volume state $f=0.0608$; ●: linear polymers; ●: $P \approx 3.6$; ○: $P \approx 6$; ○: $P \approx 15$; □: $P \approx 20$; △: $P \approx 30$; ○: $P \approx 40$. The broken line represents results for polymers having M_s of about 55,000.

covered in this study. However, it was found for branched polyvinyl acetates by Long *et al.*,⁴⁵ for star polybutadienes by Kraus *et al.*,⁴⁶ and for star polyisoprenes by Graessley *et al.*⁴⁷ that η_0 of branched polymers having long branches was higher than that of the corresponding linear polymers. As can be seen from the above figure, η_0 of star polymers with P of near 15 is proportional to $M_w^{4.5}$ at high molecular weights. Similarly, Fujimoto and coworkers found^{36,37} that η_0 of comb-shaped polystyrene was proportional to $M_w^{4.3}$, when P was constant. These results show the possibility of higher viscosity of branched polymers at very high molecular weights.

The broken curve in Figure 14 represents η_0 for star polymers having constant M_s of 55,000. This curve does increase much less rapidly with increasing molecular weight as compared with the other curves. A similar

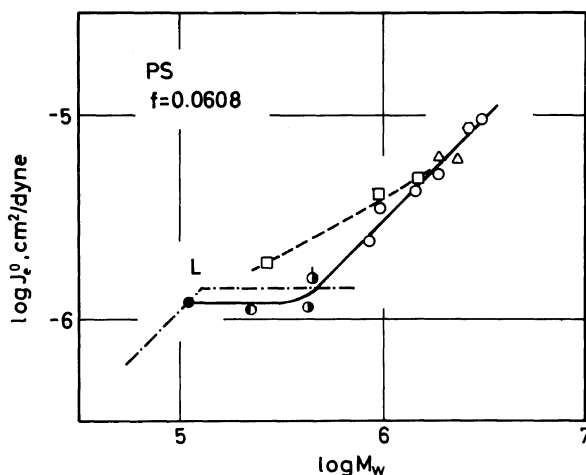


Figure 15. Molecular weight dependence of steady-state compliance J_e^0 for multi-branched polystyrene in the iso-free-volume state, $f=0.0608$. The marks are the same as those in Figure 14. The chain lines indicate results for linear polystyrenes.

behavior was observed for comb-shaped polystyrenes having branches with a constant length³⁶ and also for concentrated solutions of randomly branched polystyrenes having a constant molecular weight between branch points.⁴⁸ Such a relation between η_0 and M_w is very similar to that between $[\eta]$ and M_w for star polymers having branches with a constant length (Figure 2). However, η_0 for star polymers is almost constant at P between 3 and 7 and then it increases gradually with increasing number of branches.

Steady-State Compliance

Another parameter which determines the terminal zone is the steady-state compliance J_e^0 defined by the following

$$J_e^0 = \lim_{\omega \rightarrow 0} \left[\frac{G'(\omega)}{G'^2(\omega) + G''^2(\omega)} \right] \quad (17)$$

In Figure 15 the molecular weight (M_w) dependence of the steady-state compliance J_e^0 for multi-branched star polystyrenes used in this study is shown. In this figure, a chain line indicates the result for linear polymers; a portion of the line having a slope of 1 shows prediction from the extended Rouse theory,

$$J_e^0 = \frac{2}{5} \frac{M}{cRT} \quad (18)$$

where c is the concentration expressed by g ml^{-1} . The other portion of the line indicates a constant J_e^0 of $1.4 \times 10^6 \text{ cm}^2 \text{ dyn}^{-1}$ for linear polymers having high molecular weights reported previously.³³ The marks used for star samples of different number of branches are the same as those in Figure 14. J_e^0 for a linear polymer, a filled circle on the chain line (to the extreme left), was calculated from eq 18, assuming that $P=2$ and $M_s=55,000$, while the left-black circle for a four-branched polymer was obtained by interpolating results reported by Graessley and Roovers for four-branched polystyrenes having different lengths of branches.³⁸ As is evident from this figure, when the length (or M_s) of branches is constant, J_e^0 is independent of molecular weight for $P \leq 7$, while it increases with increasing molecular weight for a higher P (≥ 7). In this figure the molecular weight (M_w) dependences of the steady-state compliance J_e^0 for star polystyrene having constant P of near 15 (\circ) and 20 (\square) are estimated from this figure. It is clear from the figure that J_e^0 for star polymers

having P of near 15 is proportional to the molecular weight, and that for star polymers having P of near 20 is less dependent on the molecular weight and tends to approach to that for the linear polymer. Although M_s of LM8 having about 20 branches is only 11,700 and lower than the molecular weight between entanglement loci,³³⁻³⁵ $M_e \approx 18,000$, its J_e° is higher than that for linear polymers having molecular weights above the critical molecular weight, M_c' , at which the molecular weight dependence of J_e° changes from $M_w^{1.0}$ to M_w^0 . This result is inconsistent with the well-known fact that J_e° for linear polymers obeys the extended Rouse equation^{34,35} at molecular weights lower than M_c' .

As is seen from Figure 15, J_e° for star polymers having P higher than 13 can be represented by a straight line having the slope of 1.0 in the region where J_e° is proportional to M_w , irrespective of the length and number of branches. Moreover, it is noticed that J_e° for star polymers in the molten state is equal to or higher than that for linear polymers. A similar result was reported by Fujimoto *et al.*^{36,37} for comb-shaped polystyrenes. Such a result deviates from the theoretical prediction^{49,50} that J_e° for star polymers should depend on P and is lower than that for the corresponding linear polymer with the same molecular weight.

Viscoelastic Parameters in the Rubbery Zone

The viscoelastic parameters which characterize the rubbery plateau zone are the quasi-equilibrium rigidity G_{eN}° , its reciprocal J_{eN}° , entanglement compliance. The former corresponds to the height of rubbery plateau. G_{eN}° was often evaluated by integration³⁵ of G'' over the values of $\ln \omega$ encompassing of G'' :

$$G_{eN}^\circ = \frac{2}{\pi} \int_{-\infty}^a G''(\omega) d \ln \omega = 1/J_{eN}^\circ \quad (19)$$

In Figure 16 the molecular weight dependence of J_{eN}° for star polymers is shown by using the same marks as those in Figures 14 and 15. The chain line labelled L represents

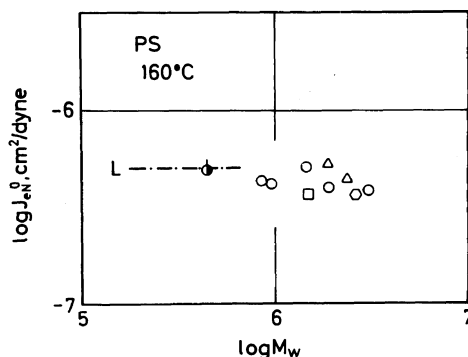


Figure 16. Molecular weight dependence of the entanglement compliance J_{eN}° for multi-branched polystyrenes at 160°C. The marks are the same as those in Figure 14. The chain line is for linear polystyrenes.

linear polystyrenes.³³ As is seen from this figure, J_{eN}° for star polymers seems to be equal to that for linear polymers at P of near six and then to decrease slightly at a higher P , approaching the limiting value. As shown by the open circles in Figure 16, J_{eN}° for star polymers having about 15 branches (LM3, 6, 10, 11 and 12) is nearly constant and somewhat lower than that for linear polymers ($5.0 \times 10^{-7} \text{ cm}^2 \text{ dyn}^{-1}$).³³ Therefore, M_e for star polymers having more than 13 branches is lower than that for linear polymers. This may be caused by the existence of intramolecular entanglements besides intermolecular entanglements in star polymers. And, it is considered that the proportion of intramolecular entanglements increases as the number of branches increases above six, because the more branches a molecule has, the higher the segment density around its center becomes. However, the difference between J_{eN}° for branched and linear polymers is rather small as compared with the difference in J_e° .

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Rheological Properties of Star Polystyrenes

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