studied. The study was carried out to observe any change in behavior of the shear rate dependency of blend-solvent systems with the change in blend compositions. Figure 6 shows characteristic shear rate behavior for solutions of PPO-PS blends. The figure shows rheological behavior for solutions of a fixed total polymer concentration of 12% but with varying proportions of the two polymers as indicated by the individual curves. The highest and lowest curves represent the behavior observed for homopolymers PS and PPO in solution. The changes in shear rate dependent viscosities do not correspond linearly with the changes in proportion of the polymers in the blend. The variation in polymer blend solution behavior becomes particularly sensitive to the amount of PPO as the proportion falls below 90% PPO. This is observed to be true for the whole range of rate of shear covered in the study, which is from 50 s^{-1} to about 3×10^5 s^{-1}.

The changes brought about in the packing structure of the blend-solvent system may explain the enhanced sensitivity of shear viscosity to the changes in relative proportion of the two polymers. Solutions of PPO-PS blends in toluene are used to illustrate this point.

Most efficiently packed spheres, touching one another, occupy a volume fraction of 0.74. $c[\eta]$ is a measure of the volume fraction occupied by the polymer molecules. Therefore, we can use this quantity to approximate the relative volume fraction occupied by the two homopolymer components in solution. The intrinsic viscosities, $[\eta]$, for PPO and PS in toluene were measured to be 0.17 and 0.45 dL/g, respectively, at 25 °C. These measured intrinsic viscosities yield a value of 88% PPO required to correspond to an occupied volume fraction of 0.74 for PPO in the blend solution. Thus, a close-knit continuous structure of PPO aggregates is formed for 88% and more PPO proportion. But for PPO proportions of lower than 88%, PS molecules are increasingly able to occupy the exclusive next-neighbor positions of a continuous PPO structure. The PPO molecules are more rigid than PS molecules. Therefore the comparatively flexible PS molecules are able to alter the characteristics of the continuous PPO system quite drastically. With an increase of PS proportion, the system approaches a condition where PPO entities are suspended essentially in a continuum of PS solution. This satisfactorily explains the observed behavior of solutions of PPO-PS blends.

In conclusion, though PPO-PS blends form a homogeneous system in melts,[2] PPO likely exists in aggregated form in the case of PPO-PS blend solutions. Experimental results shown in Figures 2 and 6 confirm this view.

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Rheological Properties of Anionic Polystyrenes. 7. Viscoelastic Properties of Six-Branched Star Polystyrenes and Their Concentrated Solutions

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ABSTRACT: The viscoelastic properties of six-branched star polystyrenes and their 50 wt % (0.641 g/mL) solutions were measured and compared with those of linear polystyrene. The dependence of zero-shear viscosity η_0 and steady-state compliance $J_e°$ upon molecular weight was obtained. η_0 for six-branched polystyrene is lower than that for linear polystyrene of the same molecular weight. The values of $J_e°$ for undiluted six-branched polystyrenes and their 50 wt % solutions depend on molecular weight even in the entanglement region. The $J_e°$ values also follow the Rouse-Ham relation in the wide ranges of molecular weights; $J_e°$ for star polymers exceeds that for linear ones at higher molecular weights. The entanglement compliance $J_{eN}°$ of branched polystyrenes is the same as that of linear ones, suggesting no effect of branching on the entanglement spacing.

In the past several years, the rheological properties of melts and concentrated solutions of branched polymers which are well characterized have been investigated, and numerous data on the effect of branching on rheology have been accumulated. The rheological properties of various types of branched polymers, such as star-shaped,[1-11] comb-shaped,[12-14] and randomly branched polymers[15] have been measured. The zero-shear viscosity, η_0, of branched polymers and their solutions is lower than that of linear polymers having the same molecular weights, at low molecular weights and/or concentrations.[5-8,12,13,15] On the other hand, the viscosity of branched polymer liquids becomes higher than that of linear ones as the molecular weight of branches increases at high concentrations. This enhancement behavior of viscosity has been observed clearly for concentrated solutions and melts of various star-shaped polymers.[1,3,6,8] This behavior implies that branched polymers with long branches have longer relaxation times in the terminal zone.[6]

The steady-state compliance, $J_e°$, which represents the elastic characteristics at long times, has also been investigated, but the behavior is still ambiguous. $J_e°$ for undiluted four-branched polystyrenes[4] and comb-shaped polystyrenes[12,13] was reported to be independent of molecular weight and higher than that for corresponding linear polymers by approximately one decade at high molecular weights. Extensive investigation recently reported[8,10] shows that $J_e°$ for undiluted four-branched[8,10]

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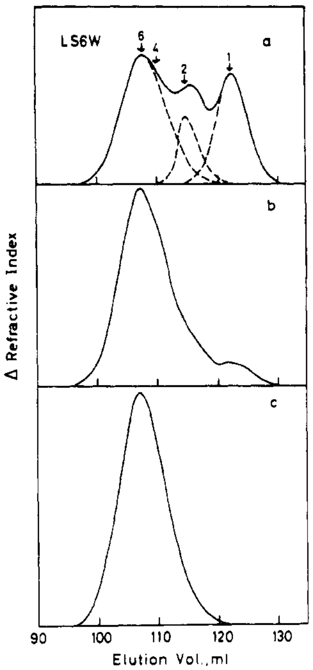

Figure 1. Gel permeation chromatograms of LS6 before the first fractionation (a), after the first fractionation (b), and after the second fractionation (c). Numbers and broken lines in a indicate number of branches and the corresponding components, respectively.

and six-branched[8] star polystyrenes is proportional to the weight-average molecular weight, M_w, over a wide range of M_w. Similar results on the molecular weight dependence of $J_e{}^\circ$ were obtained for four-branched star polystyrene solutions with concentrations of 25.5 g/dL.[5] On the other hand, for six-branched star polystyrene solutions,[5] $J_e{}^\circ$ seems to be independent of M_w, and the behavior is different from that for undiluted ones.[8]

In this paper, the viscoelastic properties for concentrated solutions (50 wt %) and melts of six-branched star polystyrenes as well as for undiluted linear polystyrenes were measured, and experimental results obtained were compared with those of four-branched and linear polystyrenes as reported in previous papers[4,15] in order to clarify the effect of the number of branches on the molecular weight dependences of various viscoelastic parameters.

Experimental Section

Materials. First, narrow-distribution living polystyrenes were prepared by anionic polymerization at low temperature near 0 °C at pressures below 10^{-6} mm, using benzene-tetrahydrofuran (THF) as solvent and *n*-butyllithium as initiator. The polymerization procedure was similar to that reported previously.[4]

A part of the polystyryl anions thus prepared was removed and purified with methanol. This is referred to as "parent polymer". The remainder was coupled with the cyclic trimer of phosphonitric chloride (CTPC)[16,17] at least for 24 h at room temperature and thereafter at 40–50 °C with stirring for about 24 h. The gel permeation chromatogram (GPC) for the unfractionated sample LS6W thus prepared is shown in Figure 1a. It is clear from this figure that the whole sample is a mixture of one-, two-, four-, and six-branched polymers.[16-18] After being precipitated and purified with methanol, the whole polymer was fractionated by precipitation in benzene–methanol in order to obtain pure six-branched polystyrene. Fractionation was performed in two or three stages. At first, a crude fractionation was repeated about 7–10 times, and then branched polymer fractions of high molecular weight were gathered and carefully refractionated until the GPC showed a single peak. The GPC was used for testing the efficiency of fractionation. The gel permeation chromatograms for LS6 before (a) and after (b) the first fractionation as well as that after the second fractionation (c) are illustrated in Figure 1. The yield of six-branched star polymers was about 16–34%. Star polymer samples thus prepared were purified with methanol and dried in a vacuum oven at 60 °C.

Table I
Molecular Weights and Coupling Ratios of the Star-Shaped Polystyrene Samples and Their Parent Polymers and Intrinsic Viscosities of Parent Polymers

		parent polymer		
sample	M_n(os)	M_n(os)	$[\eta]_l$,[a] dL/g	coupling ratio
LS8	7.91×10^5	1.37×10^5	0.326	5.8
LS7	7.31×10^5	1.17×10^5	0.292	6.2
LS11	6.44×10^5	1.06×10^5	0.265	6.1
LS1	3.61×10^5	5.89×10^4	0.211	6.1
LS6	2.45×10^5	3.95×10^4	0.168	6.2
LS5	1.44×10^5	2.31×10^4	0.123	6.2

[a] Subscript l refers to the linear polymers.

Table II
Molecular Weights, Molecular Weight Distributions, and Intrinsic Viscosities of Six-Branched Star Polystyrenes and Linear Samples

sample		M_n(os)	M_w/M_n (GPC)	M_w	$[\eta]$,[a] dL/g
star	LS8	7.91×10^5	1.29	1.02×10^6	0.496
	LS7	7.31×10^5	1.21	8.85×10^5	0.470
	LS11	6.44×10^5	1.26	8.11×10^5	0.426
	LS1	3.61×10^5	1.18	4.26×10^5	0.301
	LS6	2.45×10^5	1.29	3.16×10^5	0.268
	LS5	1.44×10^5	1.32	1.90×10^5	0.205
linear	L103	4.83×10^5	1.20	5.80×10^5	0.608
	L59	1.86×10^5	1.35	2.51×10^5	
	L102	1.12×10^5	1.21	1.50×10^5	0.304
	L106	4.99×10^4	1.22	6.14×10^4	0.194

[a] Measured in cyclohexane at 34.5 °C.

Linear polystyrenes for comparison were prepared by anionic and bulk polymerization, while four-branched polystyrenes were prepared by the coupling of polystyryl anion with $SiCl_4$, as reported in our previous papers.[4,15]

Determination of Molecular Weight and Intrinsic Viscosity. The number-average molecular weight, M_n, of the parent and star polymers was determined by the osmotic pressure technique, using a high-speed membrane osmometer. The molecular weight distribution was measured by means of a gel permeation chromatograph (GPC).

In Table I, M_n for star and parent polystyrenes, intrinsic viscosities of the parent polymers, and the coupling ratio P (ratio of M_n for the star polymer to that for the corresponding parent polymer) are shown. Coupling ratios P for all the samples are around 6.0, showing that the fractionation was satisfactory. The weight-average molecular weight, M_w, of star polymers was determined as the product of M_w/M_n evaluated from GPC and M_n determined by the osmotic pressure method. As was shown in a previous paper,[4] the weight-average molecular weights thus obtained for star polymers agreed well with those determined by the light scattering method, and we believe the M_w values in this table to be reliable. The intrinsic viscosity $[\eta]$ of all the samples was measured on dilute solutions in cyclohexane at 34.5 °C. Table II shows data obtained for star polymers and linear ones. Three undiluted samples, LS11, LS1, and LS6, and 50 wt % (0.641 g/mL) solutions of all the samples shown in Table I were used to investigate the molecular weight dependence of the viscoelastic properties. As the solvent, a partially chlorinated biphenyl, Kaneclor 500 (KC5), was used. The required amounts of polymer and solvent were dissolved in dichloromethane by stirring, and then dichloromethane was completely removed by evaporation from the mixture in a vacuum oven.

Measurement of Viscoelasticity. Measurements of the viscoelastic properties of star polymers were carried out with a concentric cylinder-type rheometer described in previous papers.[4,15] The frequency of oscillation ranged from 4×10^{-3} to 0.5 Hz. The

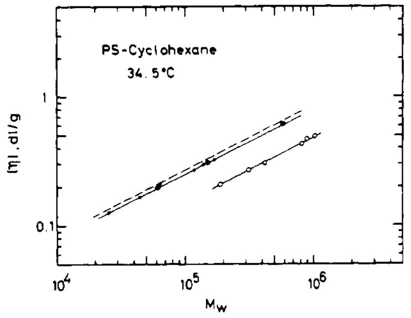

Figure 2. Intrinsic viscosity plotted against weight-average molecular weight. Open circles and small and large closed circles represent the data for star-shaped, parent, and linear polymers, respectively. The broken line indicates eq 1.

measuring temperature ranged from 30 to 180 °C. Viscoelastic functions such as the storage shear modulus G' and loss modulus G'' were calculated by use of the general equation given by Markovitz.[19] log G' vs. low ω (angular frequency) and log G'' vs. log ω curves for star polymers at different temperatures could always be superposed into respective master curves by horizontal shifts without correction for absolute temperature T and density ρ. The reference temperature is 160 °C for the bulk samples and 50 °C for the 50 wt % solutions. It was found that there was no difference between the shift factor a_T for linear polystyrenes and that for branched ones.

Results and Discussion

Dilute-Solution Properties of Star Polystyrenes. The intrinsic viscosities for linear and branched polystyrenes are plotted against M_w in Figure 2, where subscripts l and b refer to linear and branched polymers. The uppermost broken line in Figure 2 represents the viscosity equation proposed by Altares et al.[20]

$$[\eta]_l = (8.5 \times 10^{-4})M^{0.5} \tag{1}$$

for narrow-distribution polystyrenes and has a slope of 0.5. $[\eta]_l$ for parent and linear polymers (small and large closed circles in Figure 2, respectively) is well represented by

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

Figure 2 shows that the relation between $[\eta]_l$ and M_w deviates slightly from eq 1, indicated by the broken line, suggesting that linear polymers used in this study show a little polydispersity.[21] $[\eta]_b$ for six-branched star polymers having coupling ratios near 6.0 gives the bottom line of the same slope, expressed by

$$[\eta]_b = (4.8 \times 10^{-4})M_w^{0.5} \qquad (P = 6) \tag{3}$$

Therefore, the ratio of the intrinsic viscosity for six-branched star polymer to that for linear polymer of the same molecular weight, $g_\eta^{\,3} = [\eta]_b/[\eta]_l = 0.61$, can be estimated from eq 2 and 3. This value coincides well with results reported by Roovers et al.[22] and by Meunier et al.[23]

According to Zimm and Stockmayer,[24] the ratio of the mean-square radius by gyration $\langle S^2 \rangle$ for a star-branched polymer having branches of the same length to that for the corresponding linear polymer is given by

$$g_s^{\,2} = \langle S^2 \rangle_b / \langle S^2 \rangle_l = (3P - 2)/P^2 \tag{4}$$

which is identical with the g_l parameter defined by Ham.[25] For six-branched star polymers, g_s equals 0.666. As a result, the relation between g_s and g_η is $g_s = g_\eta^{\,2.5}$. This result differs slightly from the Zimm–Kilb theory,[26] expressed by $g_s = g_\eta^{\,3}$.

Frequency Dependences of Viscoelastic Functions. Master curves of log G' vs. low ω and log G'' vs. log ω for undiluted star polymers are shown in Figures 3 and 4, respectively. Curves for LS1 and LS6 cover the flow or terminal, rubbery, and transition zones. Since branched samples degrade at high temperature, measurements of the viscoelastic properties were carried out below 180 °C. Therefore, the flow zone could not be observed for the high molecular weight sample LS11. The molecular weight distribution of each sample measured by GPC was ascertained not to change before and after measurement of the viscoelasticity. As the molecular weight increases, the terminal zone shifts progressively to the low-frequency side, and the rubbery plateau becomes wider and wider. G' and G'' in the terminal zone are proportional to ω^2 and ω, respectively.

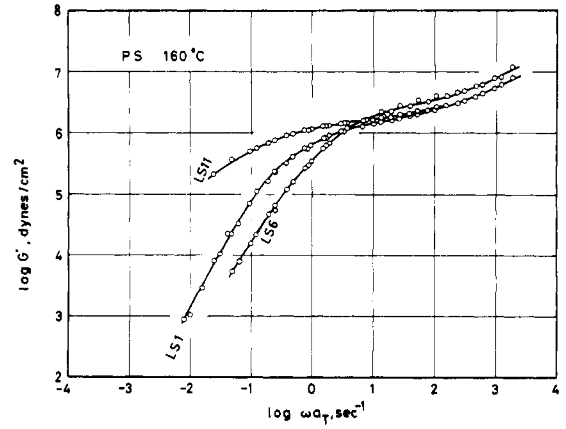

Figure 3. Frequency dependences of G' for six-branched polystyrenes, reduced to 160 °C.

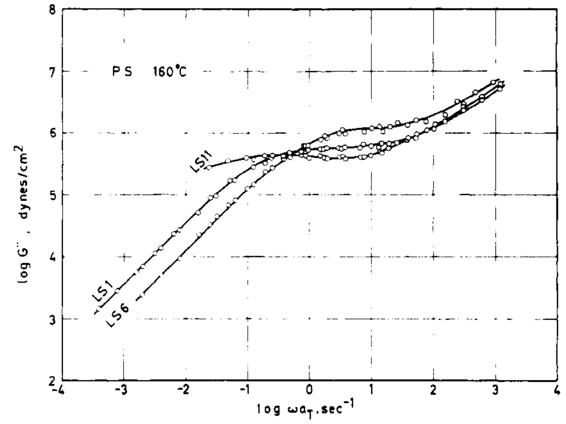

Figure 4. Frequency dependences of G'' for six-branched polystyrenes, reduced to 160 °C.

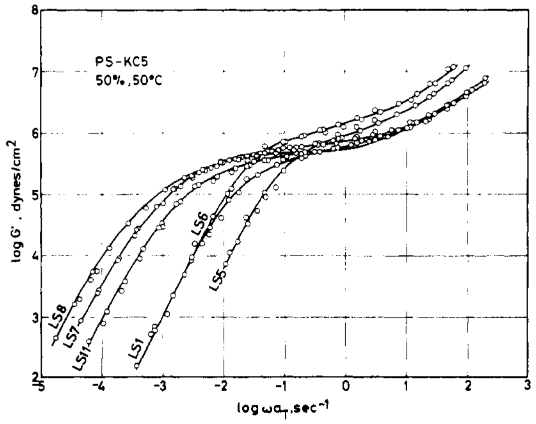

Figure 5. Frequency dependences of G' for 50 wt % solutions of six-branched polystyrenes in KC5 at 50 °C.

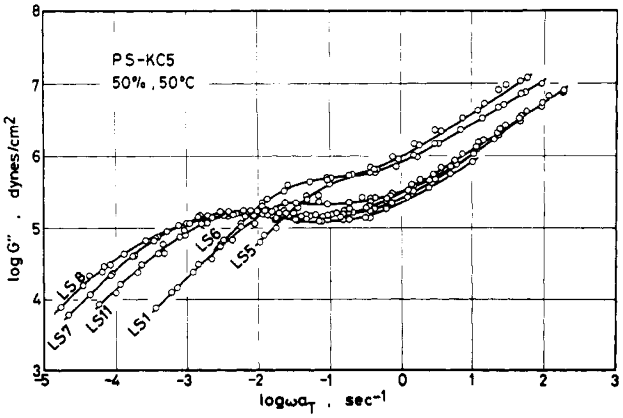

Figure 6. Frequency dependences of G'' for 50 wt % solutions of six-branched polystyrenes in KC5 at 50 °C.

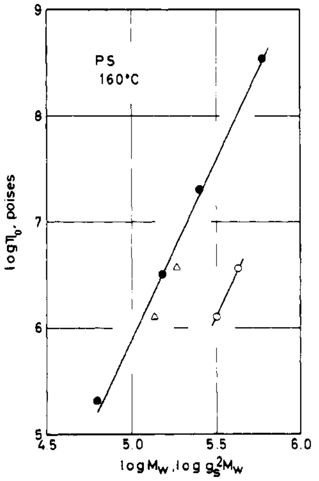

Figure 7. Zero-shear viscosity η_0 for undiluted six-branched polystyrenes logarithmically plotted against weight-average molecular weight M_w at 160 °C. Open circles indicate the data for six-branched polymers and closed circles for linear polymers. The triangles indicate the plot of log η_0 against log $(g_s{}^2M_w)$ for six-branched polystyrenes.

Figures 5 and 6 show master curves of G' and G'' for 50 wt % solutions of six-branched star polystyrenes at 50 °C. All the curves cover the flow, rubbery, and transition zones. In the transition zone, both G' and G'' values for LS5 and LS6 having low molecular weights are higher than those for the other samples having high molecular weights. Moreover, the values of the moduli do not change in the order of molecular weights. These results have never been found for linear polystyrenes[27] and are contrary to results obtained for four- and six-branched polystyrenes by Graessley and Roovers.[8] The shift of the transition zone toward the low-frequency side suggests that the samples of low molecular weight have smaller free volumes than those of high molecular weight at a constant temperature of 50 °C. After a careful examination of the measurements and calculations of the data, no experimental error was found. As will be discussed in the next section, the G'' curves of LS6 and LS5 in Figure 6 give abnormally high values of viscosity, which can be lowered by getting together of the modulus curves in the transition zone. This peculiarity of low molecular weight samples might be attributed to the difference in the temperature dependence of the free volume, though there is no complete explanation yet.

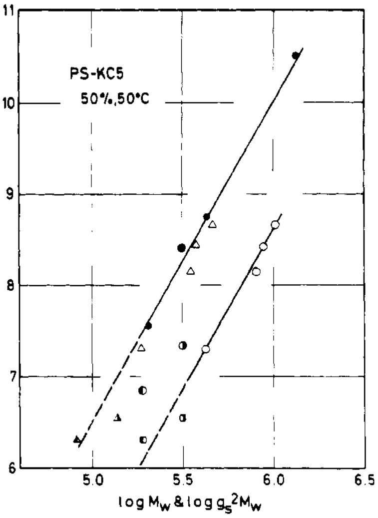

Figure 8. Zero-shear viscosity η_0 for 50 wt % (0.641 g/mL) solution of six-branched (open and half-black circles) and linear polystyrenes (closed circles) logarithmically plotted against M_w at 50 °C. The triangles indicate the plot of log $(g_s{}^2M_w)$ for six-branched polystyrene.

Viscosity–Molecular Weight Relationship. In Figure 7 the molecular weight (M_w) dependence of the zero-shear viscosity η_0 for undiluted six-branched polystyrenes (open circles) is compared with that for linear polymers (closed circles), where η_0 is defined as

$$\eta_0 = \lim_{\omega \to 0} [G''(\omega)/\omega] \tag{5}$$

Star polymers show lower η_0 in the entire range of molecular weight covered in this study. η_0 for both the linear and star polymers can be represented by straight lines having a slope of 3.5, though there are only two experimental points for the star polymers.

In Figure 8, η_0 for 50 wt % solutions of the six-branched star polystyrene at 50 °C are plotted against M_w. Small closed circles in this figure represent the data for a linear polymer prepared by bulk polymerization and reported in a previous paper.[15] The large closed circle, on the other hand, represents a result for a linear polystyrene prepared by anionic polymerization[28] and open and half-black circles show results for star polymers. For linear polymers, the molecular weight dependence of η_0 can be represented by a straight line having a slope of 3.5; η_0 is proportional to $M_w{}^{3.5}$. η_0 for six-branched star polystyrenes (open circles) is also proportional to $M_w{}^{3.5}$ at higher molecular weights. The values of η_0 for two samples of low molecular weight, LS5 and LS6, however, are extraordinarily high as shown by half-black circles. As mentioned before, the transition zone of the master curves of G'' for LS5 and LS6 are located on the low-frequency side as seen from Figure 6. If we shift the G'' curves for LS5 and LS6 in the transition zone to the high-frequency side and superpose onto those for the other samples, η_0 for LS5 and LS6 represented by half-black squares fall on the extension (broken line) of the line for samples of high molecular weight. This suggests that if the molecular weight of branches is low, six-branched star polystyrene solutions have lower free volumes as compared with high molecular ones at a constant temperature. At present, the origin of this behavior is unclear and we only mention that similar behavior has been observed for randomly branched polystyrenes studied before.[15] For the complete explanation, very careful experiments on the temperature dependence of the viscoelastic behavior should be required.

The zero-shear viscosity η_0 for undiluted six-branched polystyrenes and their 50 wt % solutions are logarithmically plotted against corrected molecular weight, $g_s{}^2M_w$,

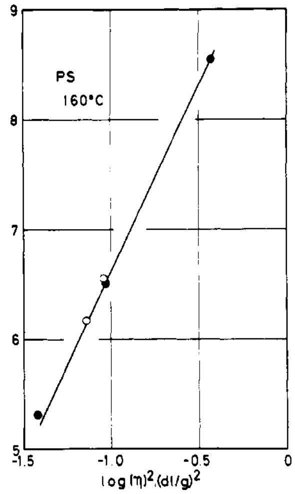

Figure 9. Zero-shear viscosity η_0 for undiluted six-branched (open circles) and linear polystyrenes (closed circles) logarithmically plotted against the square of intrinsic viscosity.

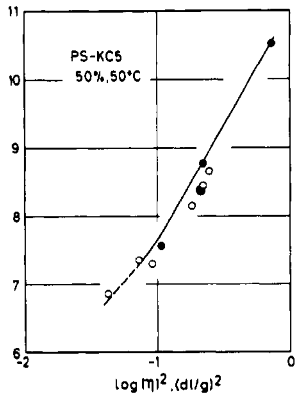

Figure 10. Zero-shear viscosity η_0 for 50 wt % solutions of six-branched (open circles) and linear polystyrenes (closed circles) logarithmically plotted against the square of intrinsic viscosity.

in Figures 7 and 8 with triangles, respectively. Such a plot is based on the theoretical consideration by Bueche[29] that the ratio of the viscosity of branched polymers to that of linear ones depends only on the radius of gyration. As is seen from these figures, the log η_0 vs. log $(g_s^2 M_w)$ plot for star polystyrenes is somewhat lower than that for linear polymers (closed circles). Similar results were reported by Graessley et al.[6] for solutions of star-branched polyisoprene having low molecular weights. It was reported by Kraus et al.[1] for melts of star-branched polybutadiene and by Berry and Fox for star-branched polystyrene[30] that Bueche's theory could be applied. On the other hand, Fujimoto et al. reported[12,13] that η_0 for comb-shaped polystyrenes did not obey Bueche's theory.

If the Zimm–Kilb relationship, $g_s = g_\eta^3$, can be applied and $[\eta]$ measured in Θ solvents is proportional to $M^{1/2}$, η_0 can be expressed by

$$\eta_0 = f(g_s^2 M_w) = F([\eta]^2) \tag{6}$$

The relation between log η_0 and log $[\eta]^2$ for undiluted six-branched star polystyrenes and their 50 wt % solutions is shown by open circles in Figures 9 and 10, respectively. As is seen from Figure 9, the relation for undiluted star polymers (open circles) is in excellent agreement with that for linear ones (closed circles). Similar results were reported by Graessley et al.[6,8] for star polymers. On the other hand, values of η_0 for 50 wt % solutions of star polymers shown in Figure 10 (open circles) are somewhat lower than those of 50 wt % solutions of linear polymer prepared by bulk radical polymerization (small closed circles), but they agree very well with that of 50 wt % solution of the linear polymer prepared by anionic polymerization (large closed circle). For the bulk polymer, $[\eta] = (7.1 \times 10^{-4}) M_w^{0.5}$ holds, as reported in a previous paper,[15] and for the anionic polymer, $[\eta] = (7.9 \times 10^{-4}) M_w^{0.5}$ (eq 2) holds as discussed above. Then, $[\eta]$ for former is lower than that for the latter at the same M_w, because $[\eta]$ depends upon the molecular weight distribution.[21] In general, the zero-shear viscosity η_0 can well be expressed by using M_w independently of molecular weight distribution. Therefore, when one compares star polymers with linear ones in their η_0 expressed by intrinsic viscosity, it is essential to use $[\eta]$ for polymers having the same molecular weight distribution.

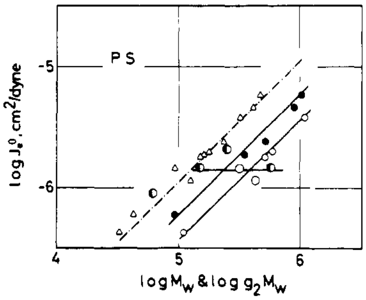

Figure 11. Molecular weight dependences of steady-state compliance $J_e°$ for undiluted six-branched (large open circles) and linear polystyrenes (half-black circles) at 160 °C. The small open circles indicate the data for six-branched polystyrenes and closed circles for four-branched polymers at 169.5 °C reported by Graessley et al.[8] The chain line shows eq 8. The triangles indicate the plot of log $J_e°$ against log $(g_2 M_w)$ for star polymers.

Molecular Weight Dependence of Steady-State Compliance. Another parameter which determines the terminal zone is the steady-state compliance $J_e°$ defined by

$$J_e° = \lim_{\omega \to 0} [G'(\omega)/G''^2(\omega)] \tag{7}$$

In Figure 11, $J_e°$ for undiluted six-branched polymers (open circles) is compared with that for the linear (half-black circles) and four-branched ones (closed circles). In this figure, large open circles represent data obtained in this study, and small open and closed circles are those observed by Graessley et al.[8] at 169.5 °C. The chain line follows the modified Rouse equation

$$J_e° = \frac{2}{5} \frac{M}{cRT} \tag{8}$$

where c (g/mL) is the concentration of the polymer in the solution.

It is well-known that $J_e°$ for linear polystyrene is independent of molecular weight, as long as its molecular weight exceeds a critical value for entanglement, M_c', while it is approximately proportional to molecular weight at lower molecular weights.[31,32] As is evident from Figure 11, $J_e°$ for six-branched polymers employed in this study is almost the same as that for the linear one of high molecular weight. The same behavior was observed for solutions of six-branched star polystyrenes.[5] However, $J_e°$ for star-branched polyisoprene reported by Graessley et al.[6] is proportional to M_w at low molecular weight. As shown in Figure 11, $J_e°$ for six-branched star polymers used in this study (large open circles) coincides almost with that for six-branched star polystyrenes reported by Graessley et al.[8] (small open circles), indicating that $J_e°$ for undiluted six-branched polystyrenes increases with increasing molecular weight. This behavior differs from that for

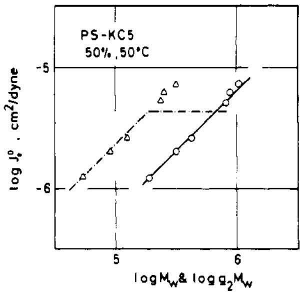

Figure 12. Molecular weight dependences of steady-state compliance $J_e°$ for 50 wt % solutions of six-branched polystyrenes (open circles) at 50 °C. The chain line represents the molecular weight dependence of $J_e°$ for 50 wt % solution of linear polystyrene, estimated from the concentration dependences[28] and the modified Rouse equation (8). The triangles indicate the plot of log $J_e°$ against log (g_2M_w) for star polymers.

Table III
Numerical Values of Zero-Shear Viscosity η_0, Steady-State Compliance $J_e°$, and Entanglement Compliance $J_{eN}°$ at 160 °C for the Six-Branched Polystyrenes at the Undiluted State

sample	M_w	η_0, P	$J_e°$, cm²/dyn	$J_{eN}°$, cm²/dyn
LS1	4.26×10^5	3.55×10^6	1.15×10^{-6}	4.96×10^{-7}
LS6	3.16×10^5	1.27×10^6	1.46×10^{-6}	5.26×10^{-7}

comb-shaped polystyrene studied by Fujimoto et al.,[12,13] who report that $J_e°$ is independent of M_w and about 10 times higher than that for linear polymers, being similar to the case of four-branched star polystyrenes reported in our previous paper.[4]

$J_e°$ for 50 wt % solutions of six-branched polystyrenes at 50 °C is shown in Figure 12. The horizontal part of the chain line at higher molecular weights represents values deduced from the concentration dependence of $J_e°$.[28] On the other hand, the ascending part of the line having a slope of 1 at lower molecular weights follows the modified Rouse equation (8). As is evident from Figure 5, the master curve of the storage modulus G' for 50 wt % solutions of six-branched polystyrenes manifests the rubbery plateau clearly, indicating that concentrations and molecular weights of samples covered in this study are higher than the critical concentration c_c and molecular weight for entanglement M_c. As is seen from this figure, however, $J_e°$ for star-branched polystyrenes is proportional to M_w in the region of $M > M_c$. It is also higher than that for their linear counterparts at high molecular weights but lower than that for linear ones at low molecular weights.

In Figures 11 and 12, $J_e°$ for undiluted star polymers and 50 wt % solutions of six-branched star polymers is plotted against g_2M_w with triangles and compared with that calculated from the Rouse–Ham model[25,33]

$$J_e° = 0.4g_2\frac{M}{cRT} \qquad (9)$$

where

$$g_2 = (15P - 14)/(3P - 2)^2 \qquad (10)$$

As can be seen from these figures, the log $J_e°$ vs. log (g_2M_w) plot for star polystyrenes can well be represented by eq 8, though the Ham theory can be applied only to short molecules having no coupling entanglements.

Numerical values of η_0 and $J_e°$ for undiluted polymers at 160 °C and 50 wt % solutions of six-branched polystyrenes at 50 °C are tabulated in Tables III and IV, respectively.

Table IV
Numerical Values of Zero-Shear Viscosity η_0, Steady-State Compliance $J_e°$, and Entanglement Compliance $J_{eN}°$ at 50 °C for the 50 wt % Solutions of Six-Branched Polystyrenes

sample	M_w	η_0, P	$J_e°$, cm²/dyn	$J_{eN}°$, cm²/dyn
LS8	1.02×10^6	4.60×10^8	7.3×10^{-6}	1.77×10^{-6}
LS7	8.85×10^5	2.68×10^8	6.3×10^{-6}	1.85×10^{-6}
LS11	8.11×10^5	1.40×10^8	5.1×10^{-6}	1.94×10^{-6}
LS1	4.26×10^5	2.00×10^7	2.60×10^{-6}	1.46×10^{-6}
LS6	3.16×10^5	2.25×10^7	2.03×10^{-6}	
LS5	1.90×10^5	7.2×10^6	1.2×10^{-6}	

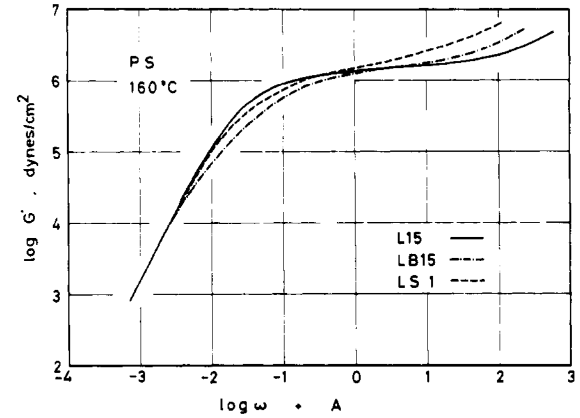

Figure 13. Comparison of G' curves for the narrow-distribution linear, four-branched, and six-branched star polystyrenes.

Viscoelastic Parameters in the Rubbery Zone. Important parameters for determining the rubbery zone are the quasi-equilibrium or entanglement modulus $G_{eN}°$ and entanglement compliance $J_{eN}°$

$$G_{eN}° = \frac{2}{\pi}\int_{-\infty}^{a} G''(\omega)\, d\ln\omega = 1/J_{eN}° \qquad (11)$$

Evaluated values of $J_{eN}°$ for undiluted star polymer at 160 °C and for 50 wt % solutions of six-branched star polymers at 50 °C are also tabulated in Tables III and IV, respectively. It is clear from these tables that $J_{eN}°$ for six-branched star polymers and their solutions is almost independent of molecular weight. The $J_{eN}°$ values of undiluted star polystyrenes agree very well with those obtained by Graessley et al.[8] at 169.5 °C, as well as with those for linear polystyrenes.[27]

Comparison of the Effect of Branching. As was emphasized in a previous paper,[4] the viscoelastic properties in the rubbery and terminal zones are strongly affected by molecular weight distribution, blending, and branching. Therefore, it is of interest to compare the effect of branching in more detail. Such a comparison has been made with the following three samples: star LS1, $M_w = 4.26 \times 10^5$, $P = 6$ ($M_s = 5.89 \times 10^4$); star LB15, $M_w = 2.48 \times 10^5$, $P = 3.7$ ($M_s = 5.63 \times 10^4$); linear L15, $M_w = 2.15 \times 10^5$, $P = 2$. M_s is the molecular weight of a branch, i.e., M_n of the parent polymer.

Frequency dependence curves of G' for these samples are shown in Figure 13, where arbitrary shifts along the abscissa have been made in order that all the curves in the terminal zone coincide with each other. Only the rubbery plateau of L15 is very flat and much wider than that of LS1, having about 2 times higher molecular weight, as well as that of LB15, having roughly equal M_w. The change from the rubbery plateau to the terminal zone for L15 occurs abruptly, but that for LS1 occurs gradually. G' for LB17 decreases more gradually with decreasing frequency

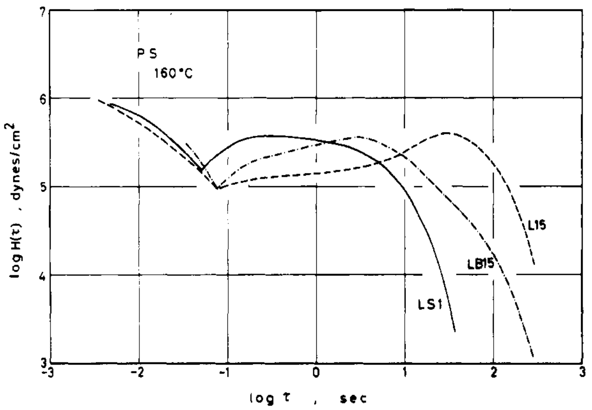

Figure 14. Comparison of relaxation spectra for the narrow-distribution linear, four-branched, and six-branched star polystyrenes.

in the rubbery flow transition region. Similar characteristic features of these samples are also clearly seen in their relaxation spectra, as determined by Tschoegl's equation[31] (Figure 14). L15 shows a clear peak in the rubbery flow transition region, and LB15 and LS1 have a broader peak at shorter relaxation times. The longest relaxation time for LS1 is shorter than those for LB17 and L15 in spite of its higher molecular weight.

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