Concentration Dependence of Viscoelastic Properties of a Mixture of Three- and Four-Branched Star Polystyrenes*

Toshiro MASUDA, Yasuhiko OHTA, Mitsunobu KITAMURA, Masahiko MINAMIDE, Kyoko KATO, and Shigeharu ONOGI

*Department of Polymer Chemistry, Kyoto University,
Kyoto 606, Japan.*

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ABSTRACT: Viscoelastic properties of concentrated solutions of a mixture of three- and four-branched polystyrenes were measured by means of a concentric cylinder type rheometer. The Vogel parameters, α_f and T_0 , were calculated from the temperature dependence of viscosity and the shift factor a_T . From the frequency dependence of the storage shear modulus G' and the loss modulus G'' , the characteristic parameters in the terminal zone such as zero-shear viscosity η_0 and steady-state compliance J_e^0 were evaluated. The dependence of these parameters on concentration was compared with that of concentrated solutions of linear polystyrenes. The concentration dependence of η_0 for star polymers is very similar to that for linear ones. However, J_e^0 for the mixture of three- and four-branched polystyrenes showed unusual behavior that was quite different from that of linear polymer and monodisperse star polymer. The entanglement compliance is also discussed.

KEY WORDS Viscoelasticity / Polystyrene / Branched Polymer / Viscosity / Steady-State Compliance / Vogel Parameters / Concentration Dependence /

In our previous papers, the rheological properties in the rubbery and flow regions of concentrated solutions and melts of star-shaped polystyrene mixtures^{1,2} and randomly branched polystyrenes³ were investigated. In these experiments, we noted the unusual behavior that the steady-state compliance J_e^0 of concentrated solutions of mixtures of three- and four-branched polystyrenes is much *lower* than those of the undiluted ones.¹ Moreover, J_e^0 for 90 wt% solutions was independent of molecular weight, but that of 50 wt% solutions proportionally increased with molecular weight in the entanglement region.² This behavior of J_e^0 observed for mixtures² is quite different from that for linear polymers⁴⁻⁹ and also from star-shaped polymers with no distribution in the number and length of branches.¹⁰⁻¹⁷

In the present paper, the dynamic viscoelastic properties for concentrated solutions of mixtures of three- and four-branched star polystyrenes have been measured to determine the concentration dependence of parameters⁵ such as the Vogel tempera-

ture T_0 , temperature coefficient of free volume α_f , zero-shear viscosity η_0 , and steady-state compliance J_e^0 . The experimental results were compared with those for concentrated solutions of linear polystyrenes.^{9,17}

EXPERIMENTAL

Materials

One (LB17) of the star-shaped polystyrene samples used in a previous study,¹ which was a mixture of three- and four-branched polymers, was taken for this study. The preparative procedure of this star polystyrene is the same as that described before^{1,2} and was not repeated. The gel permeation chromatograms and the sedimentation patterns of this sample were also similar to those reported in the previous paper.² For comparison, a narrow-distribution linear polystyrene sample L50 was also examined.¹⁷ The weight- and number-average molecular weights, M_w/M_n , and the coupling ratio P (the ratio of M_n of the star polymer to that of the corresponding branch)

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Table I. Molecular weights, molecular-weight distribution and coupling ratio (the average number of branches in a molecule) of the star and linear polystyrenes

Sample	$M_n \times 10^{-5}$ os	M_w/M_n	$M_w \times 10^{-5}$	P
LB17	3.51	1.16	4.07	3.58
L50	2.76	1.08	2.98	— ^a

^a Coupling ratio is 2.00 for linear polymer.

for these samples are tabulated in Table I.

Solutions of LB17 (BC 1 series) and L50 (SC 2 series) with polymer weight fractions of 0.07, 0.10, 0.20, 0.30, 0.50, and 0.70 g g⁻¹ were prepared and subjected to viscoelastic measurements. As the solvent, Kaneclor 500 (KC5) a partially chlorinated biphenyl was used. The volume concentrations of these solutions were 0.104, 0.147, 0.284, 0.412, 0.641, and 0.832 g ml⁻¹ at 50°C, respectively.

Measurements of Viscoelasticity

The viscoelastic functions such as the storage shear modulus G' and loss modulus G'' of sample solutions were measured by means of the concentric cylinder type rheometer described in the previous papers.¹⁻⁸ The measuring frequency ranged from

4×10^{-3} to 0.5 Hz, and the temperature, from 5 to 150°C. Frequency dependence curves of G' and G'' at various concentrations were superposed into a master curve at a certain temperature T_r and then it was reduced to T_r' at which each solution was in an iso-free-volume state; the fractional free volume f was 0.0608. This value of f was obtained for the narrow-distribution linear polystyrenes in the molten state at 160°C.⁵

RESULTS AND DISCUSSION

Frequency Dependences of Viscoelastic Functions

As is well-known, the viscoelastic properties of polymer liquids depend not only on molecular weight and concentration but also on the segmental friction factor,^{18,19} which in turn depends strongly on concentration and temperature. Therefore, the concentration dependence of rheological properties of concentrated solutions should be compared at an iso-free-volume.

In Figures 1 and 2, the master curves of G' and G'' for solutions of the star-shaped polystyrene mixture (LB17) in the iso-free-volume state ($f=0.0608$) are shown. In these two figures, the notation BC107, for example, represents 7 wt% solution of LB17 in KC5. The abscissas of the figures are the reduced angular frequency ωa_T . The reference temperature T_r' corresponding to the iso-

Figure 1. Master curves of G' for solutions of star-shaped polystyrene, LB17, reduced to the iso-free-volume state, $f=0.0608$. Corresponding temperature is T_r' shown in Table II for each solution.

Figure 2. Master curves of G'' for solutions of star-shaped polystyrene, LB17, reduced to the iso-free-volume state, $f=0.0608$. Corresponding temperature is T_r' shown in Table II for each solution.

free-volume state for each solution is tabulated in Table II. The details of the temperature dependence of viscoelasticity will be discussed in the next section. As is evident from these figures, the long time end of each curve shifts to the higher frequency side and the rubbery plateau becomes lower, as the concentration decreases. The G' curves for solutions of high concentrations, including BC130 and BC120, show the rubbery plateau regions. This suggests that the critical concentration for entanglement coupling is about $w_2=0.2$ (0.284 g ml^{-1}), where w_2 is the weight fraction of the polymer in solutions. Frequency dependence curves of G'' for samples at high concentrations show a maximum in the intermediate region between the terminal and rubbery zones. Such a maximum enables us to calculate the quasi-equilibrium modulus by the integration method.¹⁹ In the terminal zone, $\log G'$ and $\log G''$ vs. $\log \omega$ curves have the slopes of 2.0 and 1.0, respectively. As the concentration decreases, the glass transition region (the high frequency end of each curve) shifts to the right.

Shift Factor a_T and Effect of Temperature

The shift factor a_T was obtained in applying the time-temperature superposition principle to the frequency dependence curves of G' and G'' for the BC 1 series. It was found that both the star and linear

polymers give the same a_T , which can be expressed by the following WLF type equation¹⁹:

$$\log a_T = \frac{-c_1'(T - T_r)}{c_2' + (T - T_r)} \quad (1)$$

where $c_1' = 1/2.303 f_r$, $c_2' = f_r/\alpha_f$, T_r the reference temperature, f_r the fractional free volume at T_r , and α_f the temperature coefficient of the fractional free volume f which is written as

$$f = \alpha_f(T - T_0) = f_r + \alpha_f(T - T_r) \quad (2)$$

The plot of $-(T - T_r)/\log a_T$ against $(T - T_r)$ for each sample could be represented by a straight line, and the slope (m) and intercept (i) were used to evaluate the Vogel temperature T_0 and α_f defined in the free-volume theory,^{18,19} according to the relations,

$$\begin{aligned} T_0 &= T_r - i/m \\ \alpha_f &= m^2/2.303 i \end{aligned} \quad (3)$$

The free volume parameters calculated at $T_r = 50^\circ\text{C}$ are tabulated in Table II. Among these parameters, c_1' and c_2' depend on T_r but α_f and T_0 do not. T_r' is the temperature at which each solution has the fractional free volume of 0.0608, the value for the undiluted polymer at 160°C .

The concentration dependences of T_r' , T_0 , and α_f

Table II. The WLF constants (c_1^r and c_2^r), the Vogel parameters (α_f and T_0), and the temperature T_r' , corresponding to $f=0.0608$ for undiluted polystyrenes (LB17 and L50) and their solutions (BC1 and SC2 series). Linear and branched polystyrenes give the same data for free volume parameters

w_2	T_r °C	c_1^r	c_2^r	$\alpha_f \times 10^4$	T_0 °C	T_r' °C
1.00	—	—	—	5.42	47.9	160.0
0.90 ^a	50	26.92	28.0	5.76	22.0	127.6
0.70	50	12.98	65.2	5.21	-14.2	102.5
0.50	50	9.09	91.5	5.22	-41.5	74.7
0.30	50	7.50	103.2	5.61	-53.2	55.2
0.20	50	6.84	103.4	6.14	-53.5	45.6
0.10	50	6.06	99.0	7.23	-49.1	35.0
0.07	50	5.45	105.8	7.53	-55.9	24.8
0.00 ^b	50	3.52	7.96	15.5	-29.6	9.6

^a Values obtained in the preceding paper.²

^b KC5 (solvent).

Figure 3. T_r' , T_0 , and α_f plotted against weight fraction of polymer in solution for undiluted star polystyrene (LB17), its solutions (BC 1 series) and the solvent.

for LB17, shown in Figure 3, indicate that T_r' and T_0 decrease with decreasing concentration at high concentrations and T_0 increases at low concentrations after passing through a minimum. α_f is almost constant at w_2 from 1.0 to 0.2. At lower concentrations, however, α_f increases sharply with decreasing w_2 and reaches the solvent value. This result is quite similar to that obtained for PMMA

previously⁸

Concentration Dependence of Zero-Shear Viscosity

The concentration dependence of zero-shear viscosity η_0 ,

$$\eta_0 = \lim_{\omega \rightarrow 0} G''/\omega \quad (4)$$

for solutions of the star polymer (BC 1 series) is shown in Figure 4. In this figure, the closed and open circles represent zero-shear viscosities for solutions at a constant temperature, $T=50^\circ\text{C}$, and in the iso-free-volume state, $f=0.0608$, respectively. The concentration c in g ml^{-1} was employed as the abscissa.

As evident from Figure 4, the concentration dependence of η_0 at 50°C (closed circles) can be represented by a smooth curve. The viscosity and the slope of the curve at high concentration are very high since the free volumes are small; for example, η_0 is proportional to c^{40} at $c=0.832 \text{ g ml}^{-1}$. η_0 in the iso-free-volume state ($f=0.0608$) shown by open circles, however, is much less dependent on the concentration.

The concentration dependence of η_0 in the iso-free-volume state for the star polymer (LB17; open circles) is compared with that for the linear polymer (L50; closed circles) in Figure 5. The concentration dependence of η_0 for the linear polystyrenes can be represented by two straight lines having slopes of

Figure 4. Concentration dependence of zero-shear viscosity η_0 for star-shaped polystyrene solutions in KC5 at 50°C (closed circles) and in an iso-free-volume state at $f=0.0608$ (open circles).

Figure 5. Concentration dependence of zero-shear viscosity η_0 for solutions of star polystyrene, LB17 (open circles) and linear polystyrene, L50 (closed circles) reduced to the iso-free-volume state at $f=0.0608$. The broken (---) and chain (—) lines represent the relations between η_0 vs. $c(2M_w/PM_L)^{0.78}$ and η_0 vs. $c(g_s^2 M_w/M_L)^{0.78}$, respectively.

4.5 and unity in the high and low concentration ranges, respectively. On the other hand, η_0 for the branched samples exhibits three regions in the concentration dependence; $\eta_0 \propto c^1$ ($c < 0.18 \text{ g ml}^{-1}$), $\eta_0 \propto c^{4.5}$ ($0.18 < c < 0.53$) and $\eta_0 \propto c^{>4.5}$ ($c > 0.53$). Thus, the star polymer shows a stronger concentration dependence of η_0 at high concentrations than the linear polymer does. The dependences of η_0 on concentration and molecular weight are represented by,^{20,21}

$$\eta_0 \propto c^\alpha M_w^\beta \quad (5)$$

With $\alpha=4.5$, $\beta=3.5$ for linear and branched systems, the ratios β/α is calculated to be 0.78. This value is the same as or near that (0.78 or 0.85) reported recently.^{17,22} Marin *et al.*²² proposed a plot of η_0 against $c(g_s^2 M)^{\beta/\alpha}$, which gives a single curve for the concentration dependence of η_0 for three- and four-branched polybutadienes as well as for the linear one. The plot of η_0 against $c(g_s^2 M_w/M_L)^{0.78}$, which is equivalent to this plot, is shown by dot-dash line in Figure 5. M_L is the molecular weight of the linear polymer L50, 2.98×10^5 , and g_s^2 was calculated by substituting $P=3.58$ into the following equation,²

$$g_s^2 = \frac{3P-2}{P^2} \quad (6)$$

The broken line in this figure represents the relation between η_0 and $c(2M_w/PM_L)^{0.78}$. P is the average number of branches in a molecule. $(2/P)$ seems to be better than g_s^2 for reduction of the concentration dependence of η_0 of the mixture of star polystyrenes.

Concentration Dependence of Steady-State Compliance

Elastic properties of polymer liquids in the flow region are characterized by the steady-state compliance J_e^0 defined by,

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'(\omega)}{G'^2(\omega) + G''^2(\omega)} \quad (7)$$

The concentration dependence of J_e^0 for the star (LB17; open circles) and linear (L50; closed circles) polystyrenes at 50°C is shown in Figure 6. These values of J_e^0 were computed by multiplying those in the iso-free-volume state (at T_r') by $(273 + T_r')\rho/(173 + 50)\rho_0$, where ρ and ρ_0 are densities of the solutions at T_r' and 50°C. The square mark in this figure indicates the value estimated by interpolation of the molecular weight dependence of J_e^0 for 0.255 g ml⁻¹ solutions of four-branched star polystyrenes reported by Utracki and Roovers.¹⁰

As is seen from Figure 6, J_e^0 for the linear polymers (L50) is proportional to c^{-2} at high concentrations and to c^{-1} at low concentrations. J_e^0 for branched polymers (LB17) is also proportional to c^{-2} and c^{-1} at higher and lower concentrations,

Figure 6. Concentration dependence of steady-state compliance J_e^0 for solutions of star-shaped polystyrene, LB17 (open circles) and linear polystyrene, L50 (closed circles). A square indicates the value of J_e^0 for 0.255 g ml⁻¹ solutions of four-branched polystyrene reported by Utracki and Roovers.¹⁰

respectively, except for extremely high concentrations where J_e^0 begins to increase abruptly with concentration. The value of J_e^0 for the undiluted star polymer (the open circle to the extreme right) is about ten times as high as the extension of the straight line of $J_e^0 \propto c^{-2}$. J_e^0 of undiluted linear polymers is always lower than that of the solutions.⁹ The value of J_e^0 obtained by extension of the straight line to the undiluted state agrees with that of J_e^0 for four-branched star polystyrenes with the same molecular weight reported by Graessley and Roovers¹² and by Isono *et al.*¹⁴ Moreover, J_e^0 for the four-branched star polymer (square)¹⁰ is a little lower than, but very near the $\log J_e^0$ vs. $\log c$ curve for the mixture of three- and four-branched polystyrenes. The behavior of J_e^0 for the mixture of star polymers shown in Figure 6 is quite different from that recently reported by Isono *et al.*,¹⁵ Marin *et al.*,²² and us,¹⁶ for monodisperse star polymers with a fixed number of branches: Isono *et al.*¹⁵ reported that J_e^0 for four-branched polystyrenes was proportional to c^{-1} at concentrations lower than 0.5 g ml⁻¹ and that the linear relationship between J_e^0 and c^{-1} may be extended to values for undiluted polymers. More recently, it has been reported for three- and four-branched polybutadienes²² and six-branched polystyrene¹⁶ that J_e^0 is inversely proportional to the concentration over a wide range of concentration including undiluted polymers.

On the other hand, the concentration dependence of the mixture of star polystyrenes which have a

distribution in the number of branches, is quite different from that of the completely monodisperse star polymers mentioned above. In a recent investigation¹⁵ on concentration dependence of J_e^0 for four-branched star and comb polystyrenes, the reduced compliances $J_{eR}(\equiv J_e^0 c RT/M)$ for these two types of branching were plotted against cM . The figure (Figure 6 in ref 15) shows that $\log J_{eR}$ vs. $\log(cM)$ relation has a horizontal part at low cM and a slope of -1 at high cM . It also shows a hump in the intermediate region of cM . In spite of the hump, the authors concluded that the J_{eR} behavior of comb polymers is the same as that of linear and star polymers. We replotted the numerical data of J_e^0 given in the table of ref 15 against concentration and found that J_e^0 depends very weakly on concentration for the comb polystyrene solutions; the slope of $\log J_e^0$ vs. $\log c$ is slightly negative and near zero. This suggests that the $\log J_{eR}$ vs. $\log(cM)$ relation should have a slope close to plus unity, which has not been observed for linear polymers and star polymers with a fixed number of branches. This unusual behavior of J_e^0 observed for the mixture of three- and four-branched polystyrenes in this study and for comb-shaped polystyrenes mentioned above may be characteristic of branched polymers with distribution in number of branches. A similar weak concentration dependence of J_e^0 has also been observed for solutions of randomly branched polystyrenes.³ We also replotted the J_e^0 data for undiluted comb-shaped polystyrenes and their concentrated solutions against molecular weight ($J_e^0 \propto M^{-1}$) for any series of samples (with a constant number of branches and a constant molecular weight of branches), while J_e^0 for undiluted polymers is independent of molecular weight.

Zero-shear viscosity η_0 in the iso-free-volume state at T_f' , steady-state compliance J_e^0 and iso-thermal viscosity η_0^{50} at 50°C are tabulated in Table III for the undiluted star polystyrene LB17 and its solutions.

In Figure 7 the concentration dependence of J_e^0 for solutions of LB17 (open circles) is shown together with those for 50 and 90 wt% solutions of branched polymers of different molecular weight (closed circles) reported in a previous paper.² The closed circle to the extreme right (90 wt%; 0.987 g ml⁻¹) indicates that the experimental points for

Table III. Zero-shear viscosity (η_0) at T_r' where $f=0.0608$, and steady-state compliance (J_e^0) and iso-thermal viscosity (η_0^{50}) at 50°C for undiluted star polystyrene LB17 and its solutions

Sample	w_2	T_r' °C	c at T_r' g ml ⁻¹	η_0 poises	J_e^0 cm ² dyn ⁻¹	η_0^{50} poises
LB17	1.00	160.0	1.000	3.05×10^7	1.70×10^{-5}	—
^a	0.90	127.6	0.964	1.85×10^7	9.50×10^{-6}	—
BC170	0.70	102.5	0.822	9.0×10^6	3.3×10^{-6}	6.3×10^{12}
BC150	0.50	74.7	0.634	1.18×10^6	4.5×10^{-6}	1.10×10^8
BC130	0.30	55.2	0.411	1.16×10^5	1.01×10^{-5}	2.45×10^5
BC120	0.20	45.6	0.285	2.4×10^4	1.4×10^{-5}	3.7×10^3
BC110	0.10	35.0	0.148	3.15×10^3	3.10×10^{-5}	2.62×10^2
BC107	0.07	24.8	0.105	1.67×10^3	4.51×10^{-5}	3.25×10

^a Data in this row are for 90 wt% solutions of the same type of star polystyrenes.² η_0 is interpolated at the same molecular weight and J_e^0 is the average value for three samples of different molecular weight.

Figure 7. Concentration dependence of steady-state compliance J_e^0 for solutions of star polystyrene, LB17. Closed circles indicate the data of 90 and 50 wt% solutions of star polystyrenes²; M_w of these samples are 595,000 (LB26), 380,000 (LB27), 200,000 (LB28), and 113,000 (LB29).

three samples of different molecular weights coincide.² J_e^0 for 90 wt% solutions is lower than that for the undiluted polymer and higher than that for 50 wt% solutions irrespective of molecular weight.

Summarizing the experimental results obtained in this and previous studies,² we can divide the concentration dependence of steady-state compliance J_e^0 for the mixture of star polymers each with a different number of branches into three types. At concentrations below 30 wt%, J_e^0 is proportional to c^{-1} , and at concentrations between 30 and 70 wt%, J_e^0 is proportional to c^{-2} . In those concentration

regions, J_e^0 is proportional to molecular weight. At higher concentrations, J_e^0 increases rapidly after passing through a minimum at about 70 wt% and is independent of molecular weight.

Viscoelastic Properties in the Rubbery Region

As seen in Figure 1, G' is not constant in the rubbery plateau. It is difficult to determine the entanglement modulus G_{eN}^0 accurately from the height of the plateau. According to Sanders *et al.*,^{19,24} G_{eN}^0 or the entanglement compliance J_{eN}^0 can be evaluated by integration of G'' over the region of $\ln \omega$ encompassing the maximum of G'' ,

$$G_{eN}^0 = 1/J_{eN}^0 = \frac{2}{\pi} \int_{-\infty}^a G'' d \ln \omega \quad (8)$$

In practice, a G'' vs. $\ln \omega$ curve is numerically integrated from $\ln \omega = -\infty$ to the maximum of G'' , and the result is doubled.⁵ The relation between J_{eN}^0 and M_e is given by

$$J_{eN}^0 = \frac{M_e}{g_N c R T} \quad (9)$$

where g_N is a front factor. This equation is analogous to the relation between the modulus and the average molecular weight between crosslinking point. The values of J_{eN}^0 evaluated by eq 8 and those of M_e by eq 9 with $g_N=1$ for the star polystyrenes are tabulated in Table IV. It is seen that J_{eN}^0 and M_e decrease with increasing concentration.

In Figure 8, the concentration dependences of J_{eN}^0 and M_e for the star polystyrene LB17 (open circles)

Table IV. Entanglement compliance (J_{eN}^0) at 50°C, converted from J_{eN}^0 in iso-free-volume state (at T_f') and average molecular weight between entanglement loci (M_e) calculated from eq 10. M_e is assumed to be independent of temperature

Sample	w_2	c at 50°C	J_{eN}^0 at 50°C	M_e
		g ml ⁻¹	cm ² dyn ⁻¹	
Star	LB17	1.00	8.83×10^{-7}	24,900
	^a	0.90	9.47×10^{-7}	25,100
	BC170	0.70	9.36×10^{-7}	20,900
	BC150	0.50	2.02×10^{-6}	34,700
	BC130	0.30	4.07×10^{-6}	45,000

^a Data in this row are for 90 wt% solutions of the same type of polystyrenes.² J_{eN}^0 and M_e are average values of the three samples.

Figure 8. Concentration dependence of entanglement compliance J_{eN}^0 and average molecular weight between entanglement loci, M_e for solutions of star-shaped, LB17 (open circles) and linear polystyrene, L50 (closed circles). The broken line has a slope of -2.24 .

and the linear polystyrene L50 (closed circles) are shown. It can be seen that J_{eN}^0 is proportional to c^{-2} and M_e is proportional to c^{-1} . Another dependence, $J_{eN}^0 \propto c^{-2.24}$ has been reported²² recently, it is difficult to determine which is more appropriate, the slope of -2.0 (upper solid line) or -2.24 (broken line). Both the linear and star polystyrenes show the same values and the same concentration dependence of J_{eN}^0 and M_e . The unusual behavior observed for J_{eN}^0 at extremely high concentrations was not observed for J_{eN}^0 .

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