perturbation produced by the individual bead is the same in both chains. Some support for this argument is provided by the fact that the intrinsic viscosities of the dimer and the 16-mer both tend to be low or high in the same solvents (*e.g.*, low in DMSO, THP, and methanol and high in water and 6 *M* urea), indicating that the solvent–solute interactions are similar for the short and the long chain. Thus although the absolute level of intrinsic viscosity may be difficult to interpret in terms of the hydrodynamic specific volume of the oligomer, the ratio $[\eta]_{16}/[\eta]_2$ may be taken as a measure of the relative chain expansion in a given solvent.

Viscoelastic Properties of Comb-Shaped Polystyrenes

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ABSTRACT: Comb-shaped polystyrenes having various numbers of branches and various molecular weights of a branch were prepared by an anionic polymerization method. The samples were fractionated, and characterized by osmotic pressure and light-scattering methods. Stress relaxation of the sample films was observed at various temperatures and the master curve was constructed by shifting the curves according to the time–temperature superposition principle. The steady-flow viscosity, the steady-state compliance, and other rheological parameters were calculated from the master curves. The molecular weight dependence and the branch density dependence of those rheological parameters were discussed based on the theories of Bueche and Graessley.

The effect of branching on viscoelastic properties of polymers has attracted a great interest of researchers because of the importance of the study in practical use of plastics. Beside the practical purpose, moreover, the study may be useful to understand the meaning of chain entanglement or the role of molecular conformation in the rheological behavior of polymers. In spite of many papers so far published,[1–9] however, no clear conclusion has been obtained concerning the effect of branching on the rheological properties. It has not even been definitely determined whether branching decreases the steady flow viscosity or not.[4,5,8,9] Reasons for lack of a clear conclusion may be various. First of all, experiments in which the samples were well characterized is scarce. Most samples used in previous works, with a few exceptions, were neither well purified nor well characterized. Considering the procedures of preparing the samples, they may have contained an amount of unbranched polymers. It is also certain that we need more systematic studies covering wide ranges of branch length and branch number.

There are various kinds of branched molecules: (1) star shaped, (2) comb shaped, and (3) randomly branched molecules. Most works have been done by using either star-shaped molecules or randomly branched molecules. In the present work, however, we report stress–relaxation data of a series of comb-shaped polystyrenes because it is possible to change both the degree of branching and the molecular weight of branch. Although the type of branching of the present samples is a comb type, however, these samples may more closely resemble star-shaped polymers than comb, because of the number and length of the branches relative to the backbone. There are not significant differences between the g_s values (defined later) calculated as star and those calculated as comb.

Samples. Reagents. The styrene monomer used was the first grade from the Katayama Chem. Co. It was fractionally distilled and dried with lithium aluminum hydride. It was then distilled *in vacuo* with benzophenone sodium and finally dried by passing through a tube of sodium mirror. Tetrahydrofuran used was the first grade from the Katayama Chem. Co. It was dried by distillation *in vacuo* in the presence of anthracene sodium.

The *n*-butyllithium was prepared by the method reported previously[10] and cumylpotassium was prepared by the method of Ziegler and Schnell.[11] Chloromethyl ether and other reagents were for laboratory use of Nakarai Chemicals, Ltd., and Katayama Chem. Co.

Preparation of Samples. The method of preparing comb-shaped polystyrenes was reported by Altares, *et al.*,[12] and also by the present authors.[13] The parent polymer was prepared by polymerization of styrene monomer with *n*-butyllithium in THF by the method of Szwarc.[14] The product was fractionated stepwise

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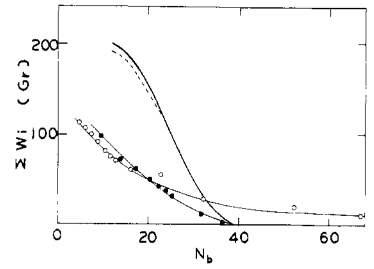

Figure 1. Examples of the comparison between the expected and experimental integral distribution curves. The graphs were obtained by adding amounts of fraction from the higher molecular weight to the lower. The solid and broken lines are the curves for series F and I, respectively, calculated using the average chlorine content. The plain and filled circles denote the experimental data of series F and I, respectively. The difference between the absolute values of calculated and experimental curves is meaningless because of the reason described in the text.

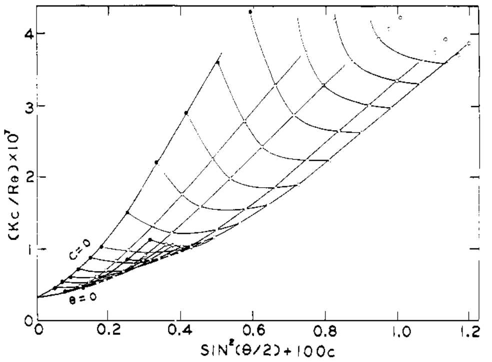

Figure 2. A typical example of the light-scattering envelope of a gellike sample. The sample was fractionated from the product obtained by coupling of polystyril anion of M_v = 12.5 × 10^4 with chloromethylated polystyrene of Cl 15.2%.

into five fractions and the center fraction was used as the parent polymer. The number average molecular weight of the parent polymer determined by osmotic pressure measurements was 9.5 × 10^4. The polystyrene was chloromethylated[15] with chloro methyl ether using stannic chloride as a catalyst. The chlorine content of the product was 0.95 ± 0.05%. The determination of the chlorine content was carried out by the method of Schöniger,[16] using a 2-l. combustion flask and 0.5-g of sample. The number average molecular weight of the chloromethylated polystyrene was also determined by osmotic pressure measurements in methyl ethyl ketone to be 9.5 × 10^4. The chloromethylated polystyrene was dissolved in benzene, freeze-dried completely under a pressure of 10^{-5} mm, and then dissolved in THF *in vacuo*.

The branch polystyrenes were also prepared by anionic polymerization of styrene monomer with cumylpotassium in THF. One part of the chloromethylated polystyrene was added to 1.3 parts of the potassium salt of the polystyril anion for coupling reaction at 0°. Since the branched polystyrene thus prepared contained uncoupled branch molecules, the product was roughly fractionated three times in benzene–methanol systems to remove the uncoupled branch molecules. The amount of the product was about 150 g.

Fractionation. Since the chloromethylation occurs at random and also since some side reactions explained below may occur in the coupling reaction, the product must have a distribution in the number of branches per molecule. Therefore, the product was fractionated stepwise into about 13 fractions in the benzene–methanol system. Among those fractions, several fractions having suitable molecular weights were used for measurements. Thus, the samples used in the present work must have no distribution in molecular weights of parent and branch polymers but must have a distribution in the number of branches per molecule.

It was often reported that if we used the lithium salt of the styril anion as the initiator, various side reactions would occur in the coupling reaction between the chloromethyl group and styril anion, resulting in the cross-linking between parent polymers.[12,17] However, it was also claimed[18] that such side reactions were negligible if potassium salt was used instead of lithium salt. Despite the fact that cumylpotassium was used as the initiator in this work, the fractionation of branched polymers showed that some fractions had molecular weights higher than those expected from the average chlorine content of the sample. That is, since the distribution of chlorine content per molecule must be expressed by a Poisson distribution, the molecular weight distribution of the branched polymer prepared can be calculated from the average chlorine content and the molecular weight of a branch. A few examples of the molecular weight distributions thus calculated are shown in Figure 1 for comparison with the integral molecular weight distributions determined from the fractionation results. (The integral amount was summed from the fraction having the highest molecular weight.) Figure 1 shows that sample series I includes no component having molecular weights higher than expected, whereas sample series F includes some fractions of molecular weights higher than expected. It is likely that fractions with molecular weights higher than expected were produced by cross-linking. This speculation on the occurrence of cross-linking was confirmed by the fact that if the chlorine content is as high as 15%, the major part of the product is cross-linked and the fractions from the product show a feature of gellike molecules[19] in their light-scattering envelopes as shown in Figure 2, though those fractions are still soluble in toluene. Therefore, the fractions having molecular weights higher than expected from the average chlorine content were not used for measurements in this work except for two samples of F-3 and H-3. Samples F-3 and H-3 have molecular weights slightly higher than the maximum, but we neglected the problem since the estimation of the expected molecular weight distribution is not so certain and no abnormality was observed in their sedimentation patterns. Strictly speaking, it is possible that if a fraction is found to have a molecular weight higher than expected, other

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TABLE I

Series	Sample no.	$M_w \times 10^{-6}$	N_b	g_s
F series	F-3	3.5_8	$52._1$	0.08_1
$M_{n,b} = 6.5 \times 10^4$	F-4	2.2_1	$32._5$	0.12_4
	F-5	1.6_4	$23._6$	0.16_4
	F-6	1.1_6	$16._4$	0.22_3
	F-8, 9	0.76_7	$10._3$	0.32_4
	F-12	0.48_8	$6._0$	0.46_7
H series	H-3	6.6_4	$50._7$	0.07_1
$M_{n,b} = 12._9 \times 10^4$	H-4	5.3_3	$40._6$	0.08_8
	H-5	3.3_1	$24._9$	0.13_9
	H-6	2.2_9	$17._0$	0.19_7
	H-8	1.4_0	$10._1$	0.30_9
I series	I-2	6.0_0	$33._6$	0.10_0
$M_{n,b} = 17._6 \times 10^4$	I-4	4.3_5	$24._2$	0.13_8
	I-5	3.1_8	$17._6$	0.18_3
	I-6	2.4_4	$13._3$	0.22_9
J series	J-1	5.2_9	$14._5$	0.20_7
$M_{n,b} = 35._8 \times 10^4$	J-2	4.7_7	$13._1$	0.22_9
	J-3	3.2_8	$8._9$	0.32_2
	J-6	2.4_0	$6._4$	0.42_9

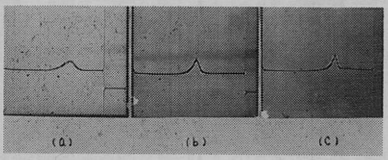

Figure 3. Examples of the sedimentation patterns of the samples: sample a, F-3; b, F-12; c, J-3; solvent, cyclohexane; temperature, 35°; concentration, 0.40%; angle, 80°; 56,100 rpm; time (a) 18 min, (b) 38 min, (c) 18 min.

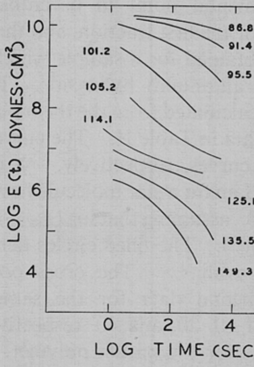

Figure 4. Typical examples of experimental relaxation modulus plotted logarithmically against time at various temperatures, sample F-4.

fractions may include cross-linked components even though their molecular weights are below the maximum expected. The possibility, however, was also assumed to be negligible in this work. These assumptions appear to cause no serious confusion in the analysis of the experimental results. Fractions used for measurements showed neither the feature of gellike molecules in their light-scattering envelopes nor any abnormal peaks in their sedimentation pattern in toluene taken by a Spinco Model E ultracentrifuge. Two sedimentation patterns of the samples having the highest and the lowest molecular weights in series F are shown in Figures 3a and b as examples. The fractions in series J contained a small number of low molecular weight components as seen in Figure 3c but the effect of the low molecular weight components was assumed to be negligible. It is desirable to calculate the molecular weight distributions of the samples from sedimentation patterns, but the molecular weight distribution cannot, at present, be calculated since we do not know the relationship between the sedimentation coefficient and molecular weight for branched molecules. In Figure 1, it should be noted that comparison between the absolute amount of fractions and the amount calculated is meaningless, since the components having low degrees of branching were lost when the uncoupled branch molecules were removed from the product.

Molecular Weight Determination. The weight average molecular weights of the fractions were determined by the light-scattering method; the details of the procedure were reported in a previous paper.[20] The number average molecular weights of branches ($M_{n,b}$) as well as that of the parent polymer were determined by osmotic pressure measurements in toluene at 25° using a Mechrolab high-speed membrane osmometer. The samples of branch molecules used for the measurements were separated from the styril anion solutions before coupling reaction. The number of branches per molecule (N_b) was calculated from those molecular weights. The molecular weights and the number of branches of all samples used in this work are listed in Table I.

Stress–Relaxation Measurements. The apparatus and the procedure for stress–relaxation measurements were the same as reported previously.[21] Films were made by evaporation of solvent from the sample solution of 10–20% in benzene on a mercury surface in a drybox. The films of 0.2-mm thickness thus prepared were dried up on a glass plate in a vacuum oven under 10^{-2} mm by raising the temperature to 120° gradually for 6 days and keeping the sample at the temperature for 24 hr. Then, the strain applied to the sample films was smaller than 1% in the glassy zone, smaller than 5% in the rubberlike zone, and smaller than 15% in the terminal zone.

Results

An example of the change in relaxation modulus with logarithmic time is shown in Figure 4. There is no qualitative difference between Figure 4 and the figures obtained for linear polymers. The correction for the change in density with temperature is taken into account in Figure 4. The density, δ, of the samples at different temperatures was assumed to be the same as those of linear polystyrene.[22]

Figure 5 shows examples of master curves for a series of branched polymers, which are obtained by shifting the curves at various temperatures according to the time–temperature superposition principle.[23] The standard temperature used (T_s) is 140°. In Figure 5, the data for monodisperse linear polystyrenes, which were estimated from the data of Tobolsky and Ako-

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TABLE II

Sample no.	τ_m, sec	E_m, dyn/cm²	η, g/cm sec	J_e, cm²/dyn
F-3	2.29×10^3	1.3×10^5	$1.9_0 \times 10^8$	7.3×10^{-6}
F-4	1.92×10^3	1.3×10^5	$1.6_0 \times 10^8$	7.2×10^{-6}
F-5	1.65×10^3	1.3×10^5	$1.3_9 \times 10^8$	6.8×10^{-6}
F-6	1.10×10^3	1.1×10^5	$1.0_1 \times 10^8$	5.7×10^{-6}
F-8, 9	6.76×10^2	1.5×10^5	$6.3_1 \times 10^7$	6.7×10^{-6}
F-12	2.49×10^2	2.1×10^5	$2.7_5 \times 10^7$	5.9×10^{-6}
H-3	4.56×10^4	1.8×10^5	$3.6_2 \times 10^9$	8.7×10^{-6}
H-4	3.22×10^4	2.5×10^5	$3.4_8 \times 10^9$	7.0×10^{-6}
H-5	1.94×10^4	2.1×10^5	$2.0_8 \times 10^9$	6.3×10^{-6}
H-6	1.15×10^4	1.9×10^5	$1.0_6 \times 10^9$	7.0×10^{-6}
H-8	8.76×10^3	1.7×10^5	$8.5_0 \times 10^8$	7.0×10^{-6}
I-2	1.21×10^5	2.0×10^5	$1.1_0 \times 10^{10}$	8.1×10^{-5}
I-4	1.01×10^5	1.9×10^5	$9.6_0 \times 10^9$	7.4×10^{-6}
I-5	7.31×10^4	1.9×10^5	$7.1_4 \times 10^9$	6.8×10^{-6}
I-6	3.49×10^4	2.2×10^5	$4.5_5 \times 10^9$	5.5×10^{-6}
J-1	1.40×10^6	2.6×10^5	$2.3_1 \times 10^{11}$	3.6×10^{-6}
J-2	1.03×10^6	2.7×10^5	$1.4_3 \times 10^{11}$	5.0×10^{-6}
J-3	6.25×10^5	2.6×10^5	$8.2_4 \times 10^{10}$	4.8×10^{-6}
J-6	3.30×10^5	2.3×10^5	$3.9_1 \times 10^{10}$	6.9×10^{-6}

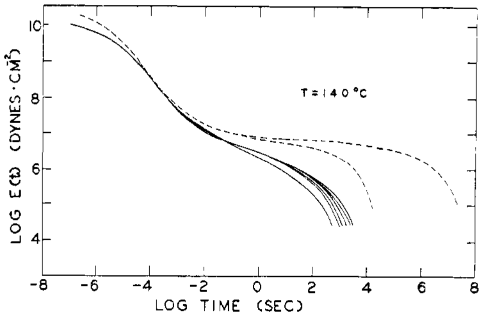

Figure 5. Master curves for series F. T_s = 140°. The solid lines denote the experimental data for samples F-3, -4, -6, -8, -9, and -12 from right to left. The right and left broken line denotes the data for linear polystyrenes which have the same molecular weights (M_w = 49 × 10⁴ and 35 × 10⁵) as samples F-3 and -12, respectively. The broken lines were estimated from the data of Tobolsy and Akovali[24,25] for monodisperse polystyrenes of various molecular weights at 100 and 129° by making use of a WLF equation reported in the papers.

vali,[24,25] are also shown for comparison. It is observed that the plateau of the branched polymers is lower than that of the corresponding linear polymers and also that the molecular weight dependence of the relaxation modulus of branched polymers at a constant molecular weight of a branch is much smaller than that of the corresponding linear polymers in the terminal zone. There is no detectable difference between the behavior of the relaxation moudulus of branched polymers and that of linear polymers in the glassy and transition regions, though the reliability of the observed values is not as high in those regions.

The shift factor a_T for all samples fit a single line independent of the density of branches and the molecular weight of a branch, as shown in Figure 6. The data are found to be close to the universal WLF equation,[23] where T_s is taken to be 140°.

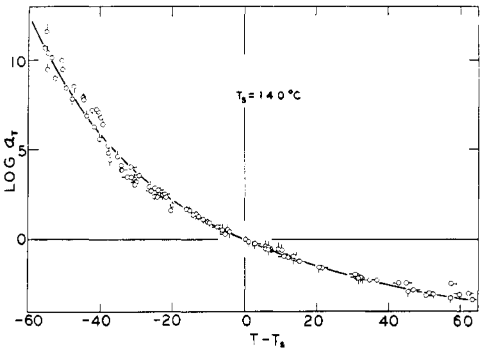

Figure 6. The shift factors for all samples: ȯ , series F; ọ , series H; -o, series I; o-, series J. The solid line denotes the universal WLF equation.[24]

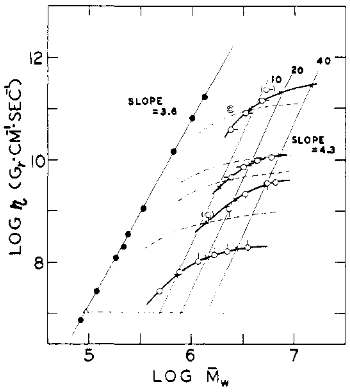

Figure 7. Molecular weight dependence of the steady-flow viscosity. Sample series, F, H, I, J, from the bottom to the top. The experimental point in parentheses in series J denotes the data for the first fraction, and that in parentheses in series H was obtained for a sample which may include a slight amount of aluminum hydroxide. The dotted lines denote the values calculated from the theory of Bueche,[35] eq 5 and 6, using the data in Table II. The curves correspond to the experimental curves, respectively. © denotes the calculated values of Ham for a star molecule having six branches of M_w = 35.8 × 10⁴, assuming that $\log(\eta_b/\eta_E) = 3.4 \log$ (original value of Ham[26]). The filled circles denote the data of Tobolsky and Akovali,[24,25] The cross points denote the estimated experimental data for the samples having the branch number of 10, 20, and 40, respectively. Δ denotes the expected value for the parent polymer. The intercepts between the horizontal broken line drawn from Δ and the experimental lines for N_b = 10, 20, 40 give M_b = 3.5, 3.8, 4.0 × 10⁴, respectively.

The steady-flow viscosity η is calculated from the stress-relaxation master curves using eq 1.[23] The

$$\eta = {}^1/_3 \int_{-\infty}^{\infty} tE(t)\, \mathrm{d} \ln t \qquad (1)$$

values of η obtained for all samples are shown in Table II and in Figure 7. It is clear that η of a branched polymer is lower than that of the linear polymer of the same molecular weight. The η increases gradually by increasing the number of branches per molecule, if the molecular weight of branch is kept constant, but the increase is much less than the increase in η of linear polymers with molecular weight. If we plot log η of

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branched polymers against log M at a constant number of branches per molecule, they fit a straight line as does log η of linear polymers. However, the slope of log η *vs.* log M plot is much higher for branched polymers (4.3) than for linear polymers (3.6).[24,25] Therefore, the present data of comb-shaped polymers should not necessarily be considered to conflict with the data of star-shaped polymers reported in the literatures.[6]

The steady-state compliance, J_e, is calculated from the master curve using eq 2.[23] The calculated results

$$J_e = \left(\frac{3}{\eta^2}\right)\int_{-\infty}^{\infty} t^2E(t)\,\mathrm{d}\ln t \qquad (2)$$

are found to be almost independent of molecular weight of branch and degree of branching as listed in Table II and shown in Figure 8. Moreover, J_e of a polymer is increased due to branching, in disagreement with the theory of Ham[26] who predicted lower values for J_e of branched polymers. In the graphical integration of eq 1 and 2, however, the data of $E(t)$ at a longer time scale were estimated from the extrapolation of the linear relationship between $E(t)$ and t.[27] The portions in η and J_e thus estimated are about 3 and 10%, respectively. Therefore, the accuracy of η and J_e obtained is determined mainly by the reliability in $E(t)$ measured. We estimate the probable uncertainties in η to be a few per cent and in J_e to be several per cent.

The maximum relaxation time τ_m and the modulus associated with the maximum relaxation time E_m, which show the behavior of the polymer in the terminal zone, are also obtained from the linear plot between $E(t)$ and t.[27] The values obtained are shown in Table II and in Figures 9 and 10, respectively. The graph of τ_m for different samples is very similar to the graph of η.

Discussion

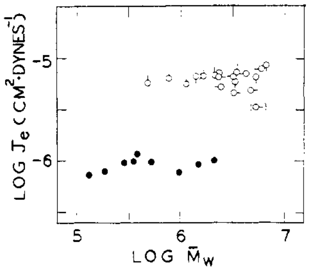

Figure 8. Molecular weight dependence of the steady-state compliance. The symbols are the same as in Figures 6 and 7.

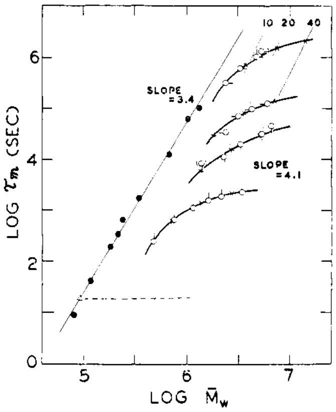

Figure 9. Molecular weight dependence of the maximum relaxation time. The symbols are the same as in Figures 6 and 7.

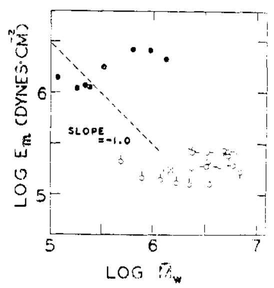

Figure 10. Molecular weight dependence of the relaxation modulus associated with the maximum relaxation time. The symbols are the same as in Figures 6 and 7.

If the concentration of a linear polymer in solution is so low that no entanglement may be assumed between the polymer chains, the viscoelastic properties of the solution was rigorously calculated by Rouse[28] and Zimm[29] using the models of free-draining and partially draining coils, respectively. The modification of the Rouse and Zimm theory for application to undiluted linear polymers, in which there are intermolecular entanglements, was carried out by Ferry, *et al.*,[30] assuming that the effective frictional coefficient of a segment increases as the 2.4th power of molecular weight. Corresponding theories on the viscoelastic properties of dilute solutions of branched polymers were published by Ham[26] and also by Zimm and Kilb.[31] That is, neglecting both hydrodynamic interaction and chain entanglement, Ham obtained the maximum relaxation time, the steady flow viscosity, and the steady-state compliance of branched polymers of various types in relation to those of linear polymers having the same molecular weights. As is clear from his assumption, his calculation corresponds to the theory of Rouse for linear polymers. On the other hand, the theory of Zimm and Kilb,[31] which took into account the hydrodynamic interaction and gave

$$[\eta_0]_b/[\eta_0]_l = g_s^{1/2} \qquad (3)$$

corresponds to the theory of Zimm.[26] Here, g_s is defined by

$$g_s = \langle S_0^2\rangle_b/\langle S_0^2\rangle_l \qquad (4)$$

$[\eta_0]$ and $\langle S_0^2\rangle$ mean the intrinsic viscosity and square radius of gyration at the θ state and the suffixes b and l imply the branched and linear polymers. The value of g_s may be estimated by a statistical calculation as was done by Zimm and Stockmayer[32] for comb-

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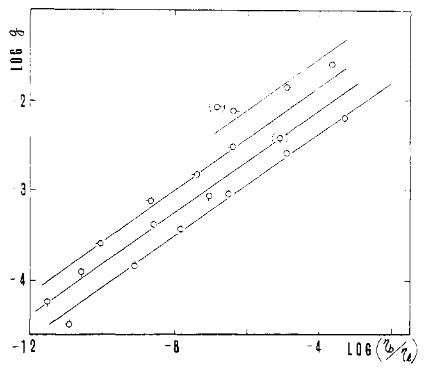

Figure 11. Plots of log (η_b/η_l) *vs.* log g_s for comb-shaped polystyrenes. The symbols are the same as in Figures 6 and 7, and the solid lines are drawn with the slope of 3.4.

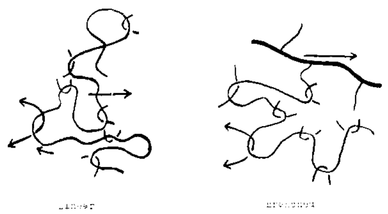

Figure 12. Schematic diagram of the entanglement between branched polymers, assumed to apply the theory of Graessley[36] to branched polymers.

shaped polymers. Orofino and Berry,[33,34] obtained

$$g_s = [p(r + 1) + 1]^{-3}[p(3p - 2)r^3 + p(p + 1)(p + 2)r^3 + p(2p + 1)(p + 1)r + (p + 1)^3] \quad (5)$$

where p and r are defined in the reference cited. The calculated values of g_s for the present samples are also shown in Table I.

If we intend to modify the theories of Ham, Zimm, and Kilb for application to undiluted polymers, as was done by Ferry, *et al.*, for linear polymers, the effective frictional coefficient of a segment would be a function of both degree of branching and molecular weight of a branch, but it is not easy to speculate the functional form experimentally. A similar discussion was given by Berry and Fox.[9]

To understand the viscosity of an undiluted branched polymer based on molecular conformation and molecular characteristics, therefore, it may be sufficient to make use of a theory which gives an molecular interpretation to entanglement as well as to viscosity of undiluted linear polymers. Such a molecular interpretation of entanglement has been presented by various workers, particularly by Bueche[35] and Graessley.[36] Based on his interpretation on entanglement, Bueche reached a conclusion that the viscosity of an undiluted branched polymer, η_b, is related to the viscosity of an undiluted linear polymer of equal molecular weight η_l by the relationship

$$\eta_b/\eta_l = g_s^{7/2} \quad (6)$$

if the branch chains are long enough to entangle each other, and if the polymers at the undiluted state have the Gaussian distribution of segments about the mass center. Thus g_s and, hence, η_b/η_l for the present samples can be calculated from eq 5 and 6, using the molecular parameters listed in Table I. If we use the data of Tobolsky and Akovali for linear polymers as a reference, therefore, we can obtain η_b for the present samples as shown in Figure 7. It is clear from the figure that the qualitative features of η_b can be well explained by Bueche's theory, but quantitative agreement is not satisfactory. Moreover, eq 6 shows that log (η_b/η_l) ought to be a single-valued function of log g_s independent of the degree of branching and the molecular weight of the branches. This speculation is not accounted for by the present experiments, as shown in Figure 11. The slopes of log (η_b/η_l) *vs.* log g_s plots are almost 3.5 but they do not fit a single line. The conclusion is the same even if we plot log η_b against log (g_sM) as suggested by Berry and Fox.[9]

Recently, a very understandable theory on the intermolecular entanglement of linear polymers was presented by Graessley.[36] He assumed that the movement of a linear polymer coil, relative to another molecule taken as an origin, is separable into two parts at the point where the molecule is entangled with the origin molecule. The center of the gravity of a longer part of the chain is assumed to move with the same velocity as the center of gravity of the molecule, whereas the shorter part of the chain must delay and later catch up the movement of the center of gravity of the molecule since the shorter part of the chain must pass through the entanglement point. By calculating the effective velocity of the chain passing through the entanglement point, the drag force exerted by the passing chain on the chain at the origin and so on, taking into account the presence of other entanglements along the passing chain, he finally reached the following equation for the steady flow viscosity of a linear polymer at zero rate of shear

$$\eta_l = K\langle S^2\rangle_l \left[1 + 0.131\left(\frac{M}{M_e}\right)^{5/2}\right] \quad (7)$$

where K is a constant and M_e is the average molecular weight between two adjacent entanglement points. The brackets in eq 7 give the molecular weight dependence of the effective frictional coefficient of a segment.

The entirely same idea can be applied to the viscosity of branched polymers. The only different idea adopted for branched polymers will be the assumption that the effective intermolecular entanglements occur only on branches and the branch can pass through the entanglement loop, while the parent chain cannot pass through the entanglement loop, as shown in Figure 12. Moreover, since the molecular weight of branches is very high, it is assumed that no entanglement occurs between the backbone chains themselves. That is, the range of integration for calculating the average drag force exerted by the passing chain on the molecule at the origin is from 0 to n_b for comb-shaped polymers, and from 0 to $n/2$ for linear polymers, n and n_b being the number of chain element in a linear molecule and in a branch, respectively. Following the calculation of Graessley on η_l, therefore, the following equation

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(33) T. A. Orofino, *Polymer*, **2**, 305 (1961).
(34) G. C. Berry and T. A. Orofino, *J. Chem. Phys.*, **40**, 1614 (1964).
(35) F. Bueche, *ibid.*, **40**, 484 (1964).
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is obtained for the viscosity of a branched polymer at zero rate of shear

$$\eta_b = K\langle S^2\rangle_b\left[1 + 0.305\left(\frac{M_b}{M_e}\right)^{5/2}\right] \qquad (8)$$

in which $\langle S^2\rangle_b$ is the square radius of gyration of the entire branched molecule and M_b is the molecular weight of the branches. Again, it is assumed that $\langle S^2\rangle_l$ and $\langle S^2\rangle_b$ in eq 7 and 8 are equal to the unperturbed values $\langle S_0{}^2\rangle_l$ and $\langle S_0{}^2\rangle_b$, respectively. Since $\langle S_0{}^2\rangle_b$ is approximately proportional to $\sqrt{M_b}$ and does not much depend on the number of branches for such highly branched comb-shaped molecules, the combination of eq 7 and 8 gives approximately the same results to η_b/η_l as eq 6 of Bueche. If unity in the braces in eq 7 and 8 is negligible compared with the other terms, the difference between two theories is mainly in the numerical factor. Therefore, the qualitative agreement of the calculated results of eq 7 and 8 with the present experimental results is as good as that of eq 6 but quantitative agreement is not satisfactory. However, it is to be noted that η_b/η_l calculated from eq 7 and 8 is not a single-valued function of g_s.

The reason for the poor quantitative agreement between the experimental results and the theory of Bueche or the extended theory of Graessley may be as follows. In both theories, it is assumed that neither M_e nor the state of entanglement is affected by the presence of branches. Because of these assumptions, both theories predict

$$\eta_b \propto M^{3.5} \qquad (9)$$

if the number of branches per molecule is kept constant. However, this prediction is not accounted for by experiments as seen in Figure 7. The data in Figure 7 show that

$$\eta_b \propto M^{4.3} \qquad (10)$$

at a constant number of branches per molecule. This fact implies that the effective frictional coefficient of a segment ζ in the undiluted branched polymer may be given by

$$\zeta = \zeta_0 M_b{}^{3.3} \qquad (11)$$

In other words, the state of entanglement in branched polymers cannot be assumed to be the same as that in linear polymers.

This conclusion immediately leads us to an expectation that if there were a linear polymer which has the same state of entanglement as the branched polymer, the ratio of the viscosity of the branched polymer to that of the imaginary linear polymer having the same molecular weight could be explained by the theories of Bueche and Graessley. To confirm this speculation, log η_b/η_l calculated from eq 7 and 8 is added to the observed values of log η_b in Figure 7 to find the viscosity of the imaginary linear polymer, $\eta_l{}^i$, which would have the same entanglement state as the branched polymer. It is observed in Figure 13 that the values of log $\eta_l{}^i$ thus calculated fit a straight line of the slope 4.9, independent of the molecular weight of a branch and the degree of branching, as expected. For the calculation, $M_e = 2 \times 10^4$ was assumed but the calculated results are not sensitive to the value of M_e since the second terms in the brackets of eq 7 and 8 are much larger than unity. However, if eq 6 of Bueche is used for the calculation of log η_b/η_l, the fit of log $\eta_l{}^i$ to a straight line is not as good as that shown in Figure 13. Here, it is to be noted that the values of g_s calculated from eq 5 do not agree with experimental values which can be determined by the light-scattering method, although the experimental results will be reported in a separate paper. Even if we use the experimental values of g_s, however, log $\eta_l{}^i$ *vs.* log M plots still fit a straight line, but the slope is a little higher.

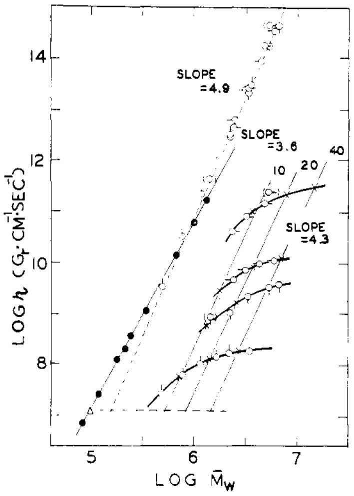

Figure 13. Analysis of the steady-flow viscosity of the branched polymers. The solid straight line denotes the data of Tobolsky and Akovali.[24,25] The dotted straight line denotes the steady-flow viscosity of imaginary linear polymer (see text).

Moreover, it is also to be pointed out that the conformation of a polymer at an undiluted state must be considerably different from the unperturbed state because of interactions among segments and, moreover, because of the requirement that an undiluted polymer must have a uniform density of segments over the solid material. In this paper, we neglect these ambiguities concerning g_s. The difference between the slope of log $\eta_l{}^i$ *vs.* log M plot (4.9) and those (4.3) of log η_b *vs.* log M at constant numbers of branches per molecule may arise either from the ambiguities in g_s or from the imperfection of eq 7 and 8, or from both. In spite of these unsolved problems, it is our opinion that the comparison between the present experimental results and the theroies of Bueche and Graessley is enough to conclude that branching of a polymer affects the viscosity of the polymer in two different ways; one is the change in the radius of gyration[37] and the other is the change in the state of entanglement. The former is calculated from the extended theory of Graessley or from the theory of Bueche, whereas the latter has not yet been calculated.

The reasons for the change in the state of entanglement due to branching are not clear but various speculations may be possible. One may be that in the application of Graessley's theory to branched polymer, the intermolecular entanglement is assumed to occur only

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(37) T. G Fox, *J. Polym. Sci., Part C*, 9, 35 (1965).

on the branches. If two polymers entangle each other on their parent backbones, the entanglement cannot be removed so easily. However, if the molecular weight dependence of the viscosity of a star-shaped polymer also has a power higher than 3.4 as was reported in the literatures,[6] this may not be the main reason. Another reason may be that, while linear polymer coils may be assumed to overlap each other extensively in undiluted polymers, the assumption cannot be justified for branched polymers. Because of the small radius of gyration and the high segment density of branched polymers, the coils cannot overlap extensively but must contact each other at the surfaces of the polymer coils.

It is observed in Figure 7 that the viscosity of a branched polymer becomes equal to the viscosity of the parent polymer at M_b = 3.5–4.0 × 10^4. If M_b is smaller than the value, there may be no effective entanglement on branches. In other words, there may be a critical molecular weight for the entanglement of branches as predicted by Berry and Fox.[9] To confirm this speculation, however, further investigations are surely required.

Finally, it should be noted that the steady-state compliance J_e of a branched polymer calculated from eq 2 is much higher than the value estimated from the quasi-equilibrium relaxation modulus, E_e, at the plateau zone. If we apply the theory of rubber elasticity to the relaxation modulus of a chain between two entanglement points, that is

$$J_e = (^1/_3E_e) = M_e/\rho RT \qquad (12)$$

we have $M_e = 2.4 \times 10^5$ from J_e in Table II and $M_e = 2.2 \times 10^4$ from E_e. This big difference may be understood if we accept the explanation of Ferry, *et al.*,[38,39] on the physical meaning of J_e, in which J_e is assumed to be the sum of two terms—the contribution of entanglement networks $J_{e,n}$ and that of the entanglement network slippage $J_{e,l}$. An increase in J_e may be caused by polydispersity of the samples used, but the increase in J_e observed in this work appears to be much higher than the increase in J_e of linear polymers due to polydispersity.[40] It is our opinion that this remarkable increase in J_e due to branching may be caused by the effect of network slippage. The branched polymers would have higher entanglement densities than linear polymers, but only at the surfaces of the polymer domains.

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Dilute Solution Thermodynamic Properties of Poly(γ-benzyl L-glutamate) in N,N-Dimethylformamide

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ABSTRACT: Osmotic pressures of dilute, isotropic solutions of fractionated poly(γ-benzyl L-glutamate) in N,N-dimethylformamide have been measured both as a function of temperature and of solute molecular weight. The osmotic second virial coefficient is found to have a temperature dependence similar to that of dilute solutions of random coils in poor solvents. A Θ temperature of *ca.* 22° is observed. The experimental data indicate that at certain temperatures the polymer–solvent system may be characterized by a χ value of up to 0.5 even though a single isotropic phase is present. This is at variance with lattice theory for rigid, impenetrable rods which predicts that any appreciable enthalpic contribution to the free energy of mixing will cause the system to separate into two phases, an isotropic phase of vanishingly small solute concentration and a concentrated anisotropic phase. Studies of phase equilibria as a function of temperature, solute concentration, and molecular weight are reported. At low solute concentrations a low-temperature gel phase is formed which does not show optical properties characteristic of the anisotropic phase that has been observed at higher concentrations.

The solution properties of synthetic polypeptides have been most frequently investigated in which these biologically important macromolecules assume randomly coiling conformations, or else the rodlike, α-helical conformation depending on the choice of solvent.[1–3] Typical is poly(γ-benzyl L-glutamate) (PBLG) which exists in the random coil state in dilute solution in dichloroacetic or trifluoroacetic acid; in other solvents such as dioxane, *m*-cresol, or N,N-dimethylformamide (DMF) the polymer is α-helical. The

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