Solution Properties of Comb-Shaped Polystyrenes

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ABSTRACT: Comb-shaped branched polystyrenes were prepared by anionic polymerization and fractionated. The ratio g_s of the mean square unperturbed radius of gyration $\langle S^2\rangle_0$ of branched polystyrene to that of linear polystyrene with the same molecular weight was determined by light scattering, as well as the similar ratio of limiting viscosity numbers at the Θ temperature g_η. The relation between g_η and g_s was found to be in agreement with the theory of Flory but in disagreement with the theory of Zimm and Kilb. The dependence of g_s and g_η on the branch density was also compared with the statistical calculations of Stockmayer, Zimm, Kurata, and Berry. Qualitatively, the agreement between calculated and experimental results is good, but quantitatively the agreement is not satisfactory.

The hydrodynamic properties of linear polymers such as viscosity, sedimentation, and diffusion are approximately determined by the radius of gyration of the polymer coil. That is, if the polymer chains act as nondraining coils, the limiting viscosity number at the Θ temperature $[\eta]_0$ is related to the unperturbed radius of gyration $\langle S^2\rangle_0^{1/2}$ and the molecular weight M by[1,2]

$$[\eta]_0 = \Phi_0 \frac{\langle S^2\rangle_0^{3/2}}{M} \tag{1}$$

where Φ_0 is a constant. In the theoretical evaluation of Φ_0, which was carried out by Kirkwood and Riseman,[2a] Zimm,[3] Hearst,[4] and Fixman,[5] the limiting viscosity number is calculated from the energy dissipation of the polymer coil at the limit of infinite hydrodynamic interaction among segments by applying the equation of Oseen to the hydrodynamic interaction. Relationship 1 is well supported by experiments.

Thus, eq 1 is believed to be applicable to branched polymers if the branched chains also act as nondraining coils. That is, the ratio of the limiting viscosity number of a branched molecule to that of a corresponding linear molecule with the same molecular weight at their unperturbed states is given by

$$[\eta]_{0b}/[\eta]_{0l} = \langle S^2\rangle_{0b}^{3/2}/\langle S^2\rangle_{0l}^{3/2} \tag{2}$$

where b and l denote the branched and linear polymers, respectively. If we define g_s and g_η by

$$g_s \equiv \langle S^2\rangle_{0b}/\langle S^2\rangle_{0l} \tag{3}$$

$$g_\eta \equiv [\eta]_{0b}/[\eta]_{0l} \tag{4}$$

eq 2 may be expressed as[6]

$$g_\eta = g_s^{3/2} \tag{5}$$

In distinct contrast to the behavior of linear polymers, however, if we employ the method of Kirkwood and Riseman[2a] and Zimm[3] to calculate the hydrodynamic properties of branched polymers, we reach a conclusion quite different from eq 5. For example, the theory of Zimm and Kilb[7] for the limiting viscosity number of star-shaped polymers at the nondraining limit is usually expressed by

$$g_\eta \cong g_s^{1/2} \tag{6}$$

In other words, Φ_0 for star-shaped polymers is not constant but a function of branching, *i.e.*, $\Phi_{0b}/\Phi_{0l} = 1/g_s$ for star-shaped polymers. Thus, study of the hydrodynamic properties of branched polymers is important from two standpoints. One is to establish a method to calculate the number and length of branches in unknown samples. This is a currently active topic in polymer characterization. The other matter of interest is to study the hydrodynamic interaction among segments by comparing the frictional coefficients of linear polymers and branched polymers. The segment density inside a polymer coil can be markedly affected by branching.[8]

A few experimental studies[9] *on star-shaped polymers* so far published implied that the theory of Zimm and Kilb (eq 6) agrees with experimental results and, consequently, the degree of branching of unknown samples is often evaluated by applying the theory of Zimm and Kilb to the limiting viscosity number. However, the branch numbers of the samples used in previous studies were usually about 3 or 4, and hence $g_s^{1/2}$ was not far from unity. In view of the error involved in the determination of $\langle S^2\rangle_0$, the conclusion cannot be considered to be definite. In fact, *it was concluded in ref 9b that eq 6 did not correlate data on comb-shaped polystyrene*, and there is a report that the limiting viscosity number and the radius of gyration of fractionated branched polystyrenes do not agree with eq 6 but rather support eq 5.[10]

In this work, therefore, we use comb-shaped poly-

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(1) P. J. Flory and T. G Fox, *J. Amer. Chem. Soc.*, **73**, 1904 (1951); P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

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(6) C. D. Thurmond and B. H. Zimm, *J. Polym. Sci.*, **8**, 477 (1952).

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(9) (a) M. Morton, T. E. Helminiak, S. D. Gadkary, and F. Bueche, *J. Polym. Sci.*, **57**, 471 (1962); (b) G. C. Berry, paper presented at IUPAC International Symposium on Macromolecular Chemistry, Tokyo-Kyoto, 1966; Preprints of Scientific Papers, **6**, 144 (1966).

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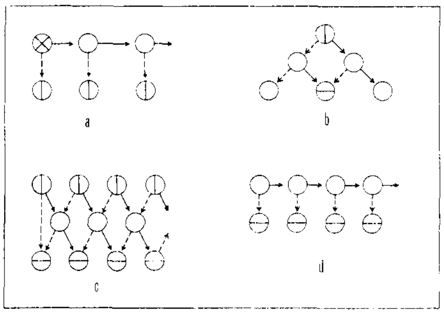

Figure 1. Fractionation scheme. The orginal sample ⊗ is fractionated by procedure a and each fraction ○ is further fractionated by the procedures appropriate to the molecular weight and the amount of each fraction: (b) for series F, (c) for series H, (d) for series I and J.

styrenes which were prepared by an anionic polymerization method. Thus we can vary the degree of branching over a much wider range than with star molecules. Since the branch length in these samples is long compared with the backbone length, however, these samples may be considered as stars rather than as combs. There is no practical difference between g_s calculated for these combs and for stars with the same number of branches. The radii of the samples in Θ solvents are determined by light scattering and compared with limiting viscosity numbers in the same solvents and also with theory. The Θ temperature is found to be only slightly affected by branching.

Experimental Section

Samples. The comb-shaped polystyrenes used here were prepared by anionic polymerization. The preparation, fractionation, and characterization methods of these samples were precisely described in a previous paper.[11] There is no great distribution in the molecular weights of backbone and branches, but there is a distribution in the number of branches per molecule. All samples were first divided stepwise into 13 fractions from toluene–methanol. These fractions were used for stress-relaxation measurements.[11] In the present work, the above fractions were further fractionated from benzene–THF–methanol by a method considered appropriate for the amount and molecular weight of each fraction. The fractionation procedures employed are shown in Figure 1. The fractions thus obtained were further purified by passing chloroform solutions of the samples through a Sephadex column to remove any traces of impurity which might remain. The samples were then freeze-dried from benzene solution and stored. The number-average molecular weights M_n were determined by a high-speed membrane osmometer (Model 502, Hewlett Packard Co.).

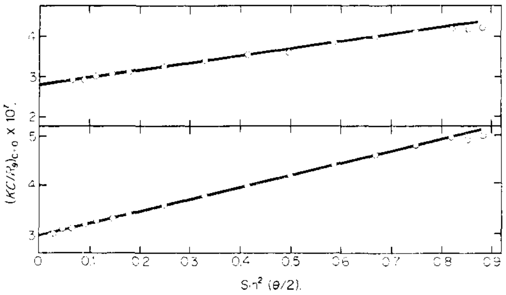

Figure 2. Examples of plots of $(KC/R_\theta)_{C=0}$ *vs.* $\sin^2(\theta/2)$: samples, upper H-4′ and lower J-2′, solvent, cyclohexane; temperature, 33°.

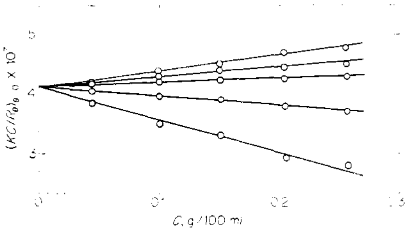

Figure 3. Examples of $(KC/R_\theta)_{\theta=0}$ *vs.* *C* plots at various temperatures: sample, H-6′; temperatures, 37, 35, 33, 30, and 28° from top to bottom.

Solvents. First-grade cyclohexane (Nagoya Katayama Chemical Co.) was passed through a silica gel column to remove aromatic impurities and fractionally distilled in the presence of metallic sodium. No impurity was detected by gas chromatography or by uv absorption.[12]

Light-Scattering Measurements. The measurement of light scattering was carried out in cyclohexane over a temperature range from 28 to 39° by using a modified Shimadzu light-scattering photometer with unpolarized 436-mμ light. Scattering data were obtained for at least five polymer concentrations at scattering angles from 18 to 140°. The solution was clarified by filtration through 0.45-μ Millipore filters. The data were analyzed according to the equation

$$KC/R_\theta = 1/MP(\theta) + 2A_2C + \cdots \quad (7)$$

$$P(\theta) = (2/u^2)\left\{u - (1 - e^{-u\lambda}) + (1 - e^{-u(1-\lambda)/f}) \times \left[f - \frac{2(1 - e^{-u\lambda})}{u\lambda/f}\right] + (1 - e^{-u(1-\lambda)/f})^2 \times \left[\frac{u\lambda - (1 - e^{-u\lambda})}{u^2\lambda^2/f(f-1)}\right]\right\} \quad (8)$$

$$u \equiv (4\pi n_0/\lambda_0)^2(Nb^2/6)\sin^2(\theta/2)$$

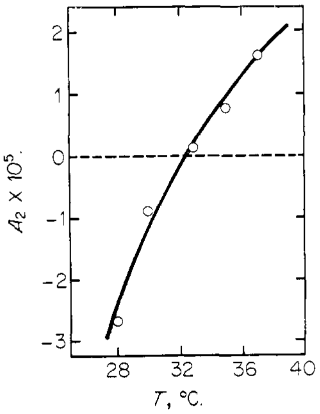

Figure 4. An example of the determination of the temperature, sample, H-6′.

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(11) T. Fujimoto, H. Narukawa, and M. Nagasawa, *Macromolecules*, **3**, 57 (1970).

(12) T. Kato, K. Miyaso, and M. Nagasawa, *J. Phys. Chem.*, **72**, 2161 (1968).

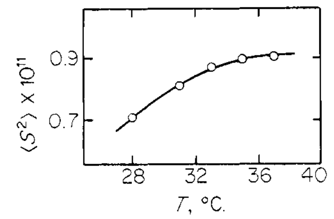

Figure 5. An example of the temperature dependence of radius of gyration, sample, H-6′.

At the limit of zero θ, eq 8 reduces to

$$P(\theta) = 1 - \frac{\langle S^2 \rangle}{3}\left(\frac{6}{Nb^2}\right)u + \cdots \qquad (9)$$

where R_θ is the Rayleigh ratio, $P(\theta)$ is the particle scattering factor for comb-shaped polymers,[13] A_2 is the second virial coefficient, K is an optical constant, f is the number of branches, λ is the fraction of the molecule in the backbone chain, λ_0 is the wavelength, n_0 is the refractive index, N is the number of segments per molecule, and b is the segment length. The data were first extrapolated to zero polymer concentration at each scattering angle to obtain $(KC/R_\theta)_{C=0}$. Then $(KC/R_\theta)_{C=0}$ was plotted against $\sin^2(\theta/2)$ to obtain $\langle S^2 \rangle_0$, as shown in Figure 2. $(KC/R_\theta)_{\theta=0}$ was also plotted against C to obtain A_2 at various temperatures as shown in Figure 3. The plots of A_2 *vs.* temperature are shown in Figure 4, from which the Θ temperatures can be determined as the values at $A_2 = 0$. The plots of $\langle S^2 \rangle_0$ *vs.* temperature are shown in Figure 5, from which the unperturbed dimension can be estimated as the value at the Θ temperature.

Limiting Viscosity Number. The limiting viscosity numbers of the samples were determined in cyclohexane at the respective Θ temperatures. The measurements were carried out by using two Ubbelohde viscometers with flow times of 315 and 325 sec at 33° and having negligibly small kinetic energy corrections. The viscosity data were extrapolated to infinite dilution by using the following equations, as shown in Figure 6. Here, η_{sp} and η_{rel} are the specific viscosity and the relative viscosity and k', k'', k''' are constants.

$$\eta_{sp}/C = [\eta] + k'[\eta^2]C + \cdots$$

$$\ln \eta_{rel}/C = [\eta] + k''[\eta]^2C + \cdots$$

$$\eta_{sp}/C = [\eta] + k'''[\eta]\eta_{sp} + \cdots$$

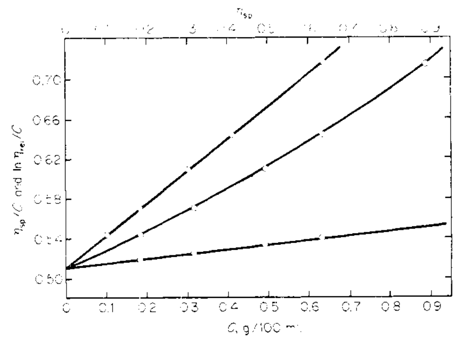

Figure 6. An example of the determination of limiting viscosity number, sample, I-7′. The lines denote plots of η_{sp}/C *vs.* C, $\ln \eta_{rel}/C$ *vs.* C and η_{sp}/C *vs.* η_{sp} from top to bottom.

Results

The weight average molecular weight M_w, the mean square unperturbed radius $\langle S^2 \rangle_0$, and the limiting viscosity number at the Θ temperature, as well as the Θ temperature of the comb-shaped polystyrenes determined, are listed in Tables I, II, and III. The ratios of the weight average molecular weight M_w to the number

TABLE I
CHARACTERISTICS OF THE SAMPLES

Series	Sample no.	$M_w \times 10^{-6}$	$M_n \times 10^{-6}$	f	Θ, °C
F series					
$(M_{n0} = 9.5_0 \times 10^4)$	5′	1.2_0	1.2_2	$16._9$	$33._0$
$(M_{nb} = 6.5_1 \times 10^4)$	11′	0.7_6	0.6_2	$10._1$	$31._3$
H series	4′	3.5_3		$26._6$	$32._0$
$(M_{n0} = 9.7_6 \times 10^4)$	5′	3.0_1		$22._6$	$31._2$
$(M_{nb} = 12._9 \times 10^4)$	6′	2.4_3		$18._1$	$32._4$
I series	4′	4.1_5		$28._7$	$31._5$
$(M_{n0} = 9.7_6 \times 10^4)$	7′	3.2_4		$17._8$	$32._0$
$(M_{nb} = 17._6 \times 10^4)$	9′	1.8_4		$9._9$	$32._8$
J series	2′	3.4_1		$9._3$	$33._0$
$(M_{n0} = 9.7_6 \times 10^4)$	5′	1.7_5		$4._6$	$32._0$
$(M_{nb} = 35._8 \times 10^4)$	8′	0.9_6		$2._7$	$33._0$

TABLE II
THE UNPERTURBED DIMENSION, THE RATIOS g_s AND THE RATIO OF THE LENGTH OF A SEGMENT IN THE BACKBONE TO THAT IN LINEAR POLYMERS α

Sample no.	$\langle S^2 \rangle \times 10^{11}$, cm^2	$(g_s)_{obsd}$	$((g_s)_{calcd})_{comb}$	$((g_s)_{calcd})_{star}$	α
H-4′	1.1_4	0.42_5	0.12	0.11	3.3
H-5′	1.0_1	0.44_1	0.13	0.12	3.1
H-6′	0.8_5	0.45_9	0.16	0.16	2.6
I-4′	1.1_8	0.37_5	0.12	0.10	3.7
I-7′	1.0_5	0.42_7	0.16	0.16	2.9
I-9′	0.7_9	0.56_3	0.26	0.28	2.4
J-2′	1.4_7	0.56_8	0.26	0.30	2.7
J-5′	0.9_9	0.74_0	0.42	0.56	2.2

TABLE III
VISCOSITY DATA

Sample no.	$[\eta]_0$	g_η	k'	$\Phi_{0b} \times 10^{21}$
F-5′	0.35_3	0.38_4	0.34_3	
F-11′	0.31_2	0.42_7	0.30_4	
H-4′	0.46_9	0.29_7	0.63_1	2.9_3
H-5′	0.44_4	0.30_6	0.34_0	2.8_4
H-6′	0.45_6	0.34_8	0.29_8	3.0_3
I-4′	0.52_1	0.30_5	0.68_7	2.8_9
I-7′	0.50_9	0.33_7	0.64_8	3.3_0
I-9′	0.50_8	0.44_6	0.28_3	2.8_7
J-2′	0.76_0	0.68_5	0.57_5	2.8_0
J-5′	0.770	0.49_7	0.55_6	3.1_7
J-8′	0.660	0.80_3	0.60_6	

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[13] E. F. Casassa and G. C. Berry, *J. Polym. Sci., Part A-2*, **4**, 881 (1966); E. F. Casassa and Y. Tagami, *ibid., Part A-2*, **6**, 63 (1968).

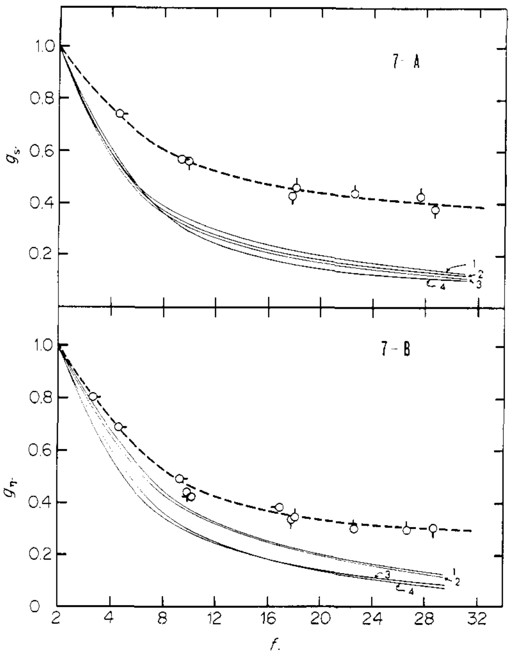

Figure 7. Relation (A) between g_s and degree of branching f and (B) between g_η and f. Samples: -O, series F; ó, series H; O-, series J; ♀, series I. The solid lines denote the values of $(g_s)_{\mathrm{comb}}$ calculated from eq 13 and those in B denote the values of $(g_\eta)_{\mathrm{comb}}$ calculated from eq 15, assuming $g_\eta = g_f^3$; $\gamma = 0.685$ (series F); $\gamma = 1.32$ (series H); $\gamma = 1.80$ (series I); $\gamma = 3.67$ (series J) from curve 1 to curve 4.

average molecular weight M_n of samples F-5′ and F-11′ are found to be nearly unity. The molecular weight distributions of the other fractions may be assumed not to be too broad for the present experiments. Sedimentation patterns of some fractions were given in a previous paper.[11] The z-average square radius of gyration determined by light scattering is also assumed to be equal to the weight-average square radius of gyration, since the difference between z-average and weight average quantities is usually smaller than the difference between weight average and number average quantities.

The number of branches per molecule f may be calculated from

$$f = (M_w - M_{n0})/M_{nb}$$

where M_{n0} and M_{nb} are the number average molecular weights of the backbone and a branch determined separately. To calculate g_s and g_η, $\langle S^2\rangle_{0l}$ and $[\eta]_{0l}$ of linear polystyrenes may be calculated from the following equations of Berry for linear polystyrenes in cyclohexane at 35°. Both equations were confirmed by our

$$\langle S^2\rangle_{0l} = 7.6 \times 10^{-18}M \tag{10}$$

$$[\eta]_{0l} = 8.4 \times 10^{-4}M^{1/2} \tag{11}$$

own experiments with NBS standard polystyrenes and other monodisperse polystyrenes.

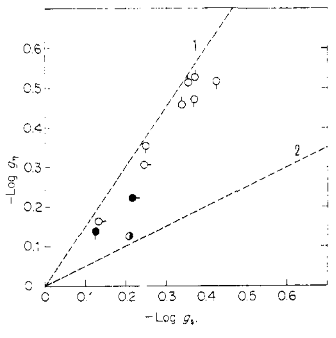

Figure 8. Logarithmic plot of g_η *vs.* g_s. The broken line 1 denotes eq 5, while broken line 2 denotes eq 6. Symbols for the samples are the same as in Figure 7. ● and ●- denote the data of Berry for comb-shaped polystyrenes (A, 53:2) and (A, 68:4), respectively. ◑ denotes the data of Berry for a star-shaped polystyrenes (A, 48:2).[9b]

In Figure 7A, the experimental values of g_s are plotted against the number of branches f. It is observed that g_s decreases with increasing f and is insensitive to the branch length. In Figure 7B, the experimental values of g_η are also plotted against f, and similar features are observed in this figure. Plots of log g_η *vs.* log g_s are shown in Figure 8, together with data from the literature, to be compared with the theory of Flory[1] and also with the theory of Zimm and Kilb[7] assuming that the samples are practically star shaped. It is clear that the theory of Flory (eq 5) shows satisfactory agreement with experiment, whereas the theory of Zimm and Kilb (eq 6) does not. The values of the Flory coefficient for branched polymers Φ_{0b} determined from eq 1 are listed in Table III. We can see that Φ_{0b} (obsd) is almost constant independent of branch number and branch length. The average value of Φ_{0b} (obsd) is 2.9×10^{22} which is close to the value accepted for linear polymers.

Discussion

The mean square radii of gyration of branched polymers and ring molecules relative to those of corresponding linear polymers of the same molecular weights, g_s, were first theoretically calculated by Zimm and Stockmayer[14] for random-flight chains with no excluded volume effect between segments. For star-shaped polymers having f branches per molecule, g_s is given by[8,14]

$$g_s = (3f - 2)/f^2 \tag{12}$$

A similar calculation for comb-shaped polymers was carried out by Casassa and Berry.[13,15] Their result is

$$g_s = (1 + f\gamma)^{-3}\{1 + 2f\gamma + (2f + f^2)\gamma^2 + (3f^2 - 2f)\gamma^3\} \tag{13}$$

where γ is the ratio of the molecular weight of a branch to that of the backbone. It is assumed in eq 13 that the molecular weights of backbone and branch and the number of branch points per backbone are homogeneous, but the distribution of branch points along the backbone is random. This model is appropriate for our samples if we may neglect the molecular weight distribution within each fraction. The calculated values of g_s from eq 13 are listed in Table II, where it is to be noted that no practical difference is found between $(g_s)_{\mathrm{comb}}$ calculated from eq 13 and $(g_s)_{\mathrm{star}}$ calculated from eq 12. That is, the present samples may practically be assumed to be star-shaped polymers. It can also be seen that eq 13 becomes identical with eq 12 when γ is very large.

(14) B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, 17, 1301 (1949).

(15) G. C. Berry, *J. Polym. Sci., Part A-2*, 6, 1551 (1968).

Calculated values of $(g_s)_{\text{comb}}$ are plotted in Figure 7A for comparison with the experimental data. We see that the calculated values are almost independent of the branch length, as are the experimental values, and show qualitatively the same decreasing tendency with increasing f as the observed ones. Quantitatively, however, the observed values are much larger than the calculated ones when the branch density is high. That is, even at the Θ temperature, the real comb-shaped polystyrene has a radius of gyration greater than that calculated by assuming the same Kuhn statistical segment as for linear polystyrenes. The same result was reported by Berry,[9b] though the difference between $(g_s)_{\text{calcd}}$ and $(g_s)_{\text{obsd}}$ for his samples was much smaller because of low density of branching in his samples.

The difference between the observed and calculated values could be caused by the effect of branches on the rotational freedom around the carbon–carbon chain of the backbone. For instance, the average molecular weight between two neighboring branch points for sample no. H-4′ is about 4000, and hence the number of the Kuhn statistical segments between two neighboring branch points is only 4 if we assume the same segment size for comb-shaped as for linear polystyrenes. Moreover it is likely that the segments around the branching points are extended even at the Θ temperature because of the high density of segments, the Θ temperature being defined as that temperature at which the overall intermolecular interaction disappears. In practice, if we plot the ratio of the observed values of $g_s((g_s)_{\text{obsd}})$ to the calculated values $((g_s)_{\text{calcd}})$ against the reciprocal molecular weight between two neighboring branch points $1/M_s$ in Figure 9, we see that the ratio increases linearly with respect to $1/M_s$ from unity at $1/M_s = 0$, irrespective of the branch length. If we assume that only the backbone is uniformly extended, we can estimate the ratio α of the length of a segment in the backbone to that in linear polymers under Θ conditions. The values of α are listed in Table II.

The observed values of g_η are plotted against the branch density in Figure 7B. It is found that g_η does not depend on the branch length but does depend on the degree of branching as does g_s. A theoretical equation for g_η for comb-shaped polymers has not yet been published. The "theoretical" values of g_η, therefore, are computed from the theoretical ratio g_f for translational frictional coefficient by assuming[8]

$$g_\eta = g_f{}^3 \tag{14}$$

The g_f for comb-shaped polymers was calculated by Kurata and Fukatsu[16] and Berry,[15] assuming nondraining coils. The equation of Berry is

$$g_f{}^{-1} = (1 + f\gamma)^{-3/2}\{1 - f\gamma^{3/2} + {}^4/_5 fT_0(\gamma) + {}^4/_{35} f(f - 1)[T_1(2\gamma) - 2T_1(\gamma)]\}$$

$$T_m(x) = (1 + x)^{m+5/2} - \left(1 + \frac{7m}{2}x^{5/2} + x^{m+5/2}\right) \tag{15}$$

The features in the comparison between theory and experiment in Figure 7B are similar to those in Figure 7A for g_s.

Table I shows that the Θ temperature for branched polymers may be different from that for linear polymers consisting of the same structural unit. The Θ temperature of a polymer may be affected by introducing different structural units such as branch points and end groups,[17] but in addition it could be affected by the steric effect of branches discussed above. However, the deviation of the Θ temperature for branched polystyrenes from that for linear polystyrenes (35° in cyclohexane) is not great enough to establish a definite relation between the Θ temperature and branching.

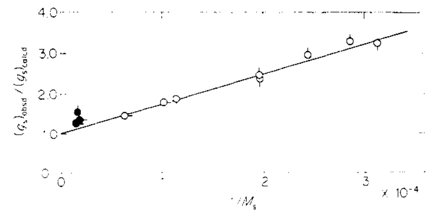

Figure 9. Relation between $(g_s)_{\text{obsd}}/(g_s)_{\text{calcd}}$ and $1/M_s$. Symbols are the same as in Figure 8.

From Figure 8, it is clear that the experimental data support eq 5 rather than eq 6. Strictly speaking, the present samples are not star but comb, and g_η for comb has not been calculated. There is, therefore, a possibility that if we would calculate g_η for combs by the methods of Kirkwood and Riseman[2a] or Zimm,[3] we might find good agreement between theory and experiment; or that if we determined g_η of true star-shaped polymers we might obtain agreement between the theory of Zimm and Kilb[7] and experiment, as for one example presented by Berry.[9b] Our present speculation, however, is that those possibilities are not high; for if we assume eq 14 and calculate the value of $g_f{}^3$ from eq 15, the calculated values are still far from the experimental results.

There is yet another possibility that the present results might not contradict the theory of Zimm and Kilb. Since even at the Θ temperature the present samples do not have conformations predicted from Gaussian statistics assuming the same statistical length as for linear polymers, there is a possibility that the Flory constant Φ_b for real branched polymers at the Θ temperature is different from that for the ideal Gaussian conformation of branched polymers Φ_{0b}. Then, we may write

$$g_\eta = (\Phi_{0b}/\Phi_{0l})(\Phi_b/\Phi_{0b})g_s{}^{3/2}$$

Since the experimental results show that eq 5 is almost valid, it turns out that

$$(\Phi_{0b}/\Phi_{0l})(\Phi_b/\Phi_{0b}) = 1$$

Thus, if $\Phi_b/\Phi_{0b} = g_s$, the present results would not disagree with the theory of Zimm and Kilb. However, it seems too fortuitous that this relationship would be always valid, though it is worthwhile to reconsider this problem when the expansion factor and limiting viscosity number of the samples are studied in good solvents.

It is important and interesting to see that the theories of Kirkwood and Riseman and Zimm, which were successfully applied to linear polymers essentially in accord with the idea of Flory, apparently fail to explain the hydrodynamic behavior of branched polymers.

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