Dilute Solution Properties of Randomly Branched Poly(methyl methacrylate). II.

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ABSTRACT: Randomly branched polydisperse polymers prepared by copolymerization of methyl methacrylate with ethylene dimethacrylate were fractionated by the fractional solution technique. Light scattering, viscosity, osmotic pressure, and sedimentation measurements were carried out on the fractionated samples. It was found that in the theta state the intrinsic viscosity of a branched molecule obeyed Zimm and Kilb's $g^{1/2}$ -rule, but in a good solvent it showed some deviation if the sample had many branch points. It was also found that the sedimentation constant of a branched molecule agreed with the theoretical value derived by Kurata and Fukatsu if the sample had a narrow molecular weight distribution.

KEY WORDS Branch / Poly(methyl methacrylate) / Molecular Weight Distribution / Intrinsic Viscosity / Sedimentation / Dilute Solution /

In the previous work,¹ we investigated the hydrodynamic properties of a randomly branched polydisperse polymer which was obtained by copolymerization of methyl methacrylate(MMA) and a small amount of ethylene dimethacrylate(EDMA). In this study, the weight-average intrinsic viscosity of the randomly branched polydisperse polymer was calculated assuming that the distribution of molecular weight and branch unit of a sample was written in the Stockmayer formula² and that the intrinsic viscosity of a monodisperse branched polymer obeyed Zimm and Kilb's theory.³ The experimentally determined intrinsic viscosities of the samples closely agreed with calculated values, at least in the theta state. Thus, it was shown that average branching could be estimated by intrinsic viscosity even if the sample had a broad molecular weight distribution. Of course, it is necessary to know, as reference, the intrinsic viscosity of linear molecules with the same weight-average molecular weight.

It was not possible, however, to obtain any details of branching from the radius of gyration and the sedimentation constant, due to the broad molecular weight distribution of the sample.

In this paper, the randomly branched polydisperse polymer was fractionated to obtain a

series of samples with narrow molecular weight distribution(MWD), and their hydrodynamic properties, intrinsic viscosity, and sedimentation constant were studied in the absence of disturbance by the molecular weight distribution. In respect of the intrinsic viscosity of branched polymers in particular it is still not clear whether Zimm and Kilb's $g^{1/2}$ -rule holds or not in a good solvent. It is important to clarify this problem, for it is easier to perform the experimental work in a good solvent than in theta solvent.

In our investigation of randomly branched poly(methyl methacrylate), we were aware that Kurata and his coworkers⁴ were studying the hydrodynamic properties of randomly branched polystyrene. Their results were in general agreement with ours.

EXPERIMENTAL

Fractionation

Among the samples detailed in the previous work a linear polymer B-0 and two randomly branched polymers B-3 and A-4, were fractionated using the fractional solution technique. The results of molecular characterization of the whole polymers are summarized in Table I.

Table I. Results of molecular characterization for whole polymers used in this work

Sample	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$\bar{\gamma}$	$\bar{n}_w$
B-0	29.6	20.9	0	0
B-3	62.0	24.1	0.523	1.094
A-0	16.2	10.5	0	0
A-4	134.0	13.2	0.879	7.25

About 600-g celite support was coated with 23-g polymer by evaporating acetone solution and packed into a 6-cm ϕ $\times$ 120-cm column. Fractions were eluted at a constant temperature 35°C, using methyl ethyl ketone (MEK)—ethanol mixture with increasing solvent power. The solvent power was changed by the batch method. For sample A-4, in order to obtain the fraction having as many branch units and as sharp a MWD as possible, it was first fractionated by the fractional precipitation technique, then some higher-molecular-weight fractions were again fractionated by the fractional solution technique. As gelation occurred at the stage of polymer recovery, the chloroform-soluble part of the fractions were recovered by centrifugation. The gelation may be caused by cross-linking of incompletely reacted EDMA. No gelation occurred for the fractions of B-3 which had less EDMA than A-4. Thus we obtained 8 fractions for the sample B-0, 12 fractions for B-3 and 3 fractions for A-4.

Light-scattering Measurements

Light-scattering measurements were carried out in MEK at 40°C. The detailed procedure was given in the previous work.

Osmometry

Osmotic pressure was measured in benzene at

37°C. Extrapolation to zero concentration was obtained by plotting π/c or $(\pi/c)^{1/2}$ against c , where π is the osmotic pressure and c is the concentration. The latter procedure was applied for the fractions with molecular weight above 400000 and a linear extrapolation was obtained.

Viscometry

The intrinsic viscosities were determined in MEK at 40°C and in acetonitrile (CH₃CN) at 38°C using a dilution viscometer of Ubbelohde type. No correction for kinetic energy was necessary in any of the measurements.

Sedimentation

Sedimentation-velocity measurements were made in acetonitrile at 38°C. As this system, *i.e.*, PMMA—acetonitrile, showed a rather high sedimentation-velocity, rotor speed was decreased from 34450 rpm to 25090 rpm, depending on the molecular weight.

Gel-Permeation Chromatography

In order to find the fractionation efficiency of the fractional solution technique, gel-permeation chromatography (GPC) of the unfractionated sample B-0 and its fractions were measured in tetrahydrofuran at room temperature using equipment from Waters Associates. Columns of gel pore size 10⁶, 10⁵, and 10⁴ Å were used.

RESULTS AND DISCUSSION

The results of light-scattering and intrinsic-viscosity measurements are summarized in Tables II and III. The results of fractionation and osmotic-pressure measurements are also given in Tables IV and V. M_w/M_n ratios are shown in the fifth column in the tables. These ratios

Table II. Results of light scattering and intrinsic viscosity measurements for fractions of B-0

Sample	In MEK 40°C			In MEK 40°C		In CH ₃ CN 38°C	
	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2}$, Å	$A_2 \times 10^4$, mol/cc g ²	$[\eta]$, dl/g	k'	$[\eta]$	k'
B-0-1	4.59	—	4.43	0.168	0.708	0.110	1.04
B-0-2	8.19	79	4.23	0.239	0.683	0.163	1.02
B-0-3	12.6	90	4.01	0.314	0.463	0.172	0.988
B-0-4	18.0	126	3.39	0.400	0.481	0.210	0.980
B-0-5	26.1	160	3.05	0.530	0.450	0.242	1.09
B-0-6	38.8	203	2.86	0.693	0.455	0.301	1.02
B-0-7	58.5	279	2.72	0.916	0.405	0.365	1.06
B-0-8	94.0	423	2.34	1.26	0.460	0.441	1.14

Table III. Results of light-scattering and intrinsic-viscosity measurements for fractions of B-3 and A-4

Sample	In MEK 40°C			In MEK 40°C		In CH ₃ CN 38°C	
	$M_w \times 10^{-4}$	$\langle S^2 \rangle_z^{1/2}$, Å	$A_2 \times 10^4$, mol/cc g ²	$[\eta]$, dl/g	k'	$[\eta]$	k'
B-3-1	4.89	—	5.02	0.162	0.590	—	—
B-3-2	8.85	—	4.61	0.248	0.482	—	—
B-3-3	12.8	—	3.29	0.341	0.590	—	—
B-3-4	17.4	70	3.20	0.432	0.435	—	—
B-3-5	27.4	171	3.16	0.538	0.451	—	—
B-3-6	36.6	213	2.90	0.647	0.445	—	—
B-3-7	46.5	218	2.67	0.745	0.372	0.314	1.03
B-3-8	59.0	237	2.58	0.864	0.419	0.337	1.03
B-3-9	114	386	2.12	1.14	0.441	0.412	1.05
B-3-10	145	445	2.27	1.24	0.395	0.435	1.05
B-3-11	215	543	2.23	1.35	0.419	0.456	1.01
B-3-12	449	836	1.95	2.01	0.449	0.612	1.04
A-4-1	147	389	1.44	0.985	0.520	0.361	0.991
A-4-2	467	731	0.92	1.42	0.575	0.478	0.925
A-4-3	699	1083	0.61	1.54	0.614	0.574	0.859

Table IV. Results of fractionation and osmotic pressure measurements for linear polymer, B-0

Sample	W , g	$M_n \times 10^{-4}$	$A_2 \times 10^4$, mol/cc g ²	M_w/M_n
B-0-1	1.143	4.15	4.43	1.11
B-0-2	1.157	7.87	4.23	1.04
B-0-3	1.786	11.5	4.01	1.10
B-0-4	2.944	15.7	3.39	1.15
B-0-5	4.709	23.5	3.05	1.11
B-0-6	5.956	35.9	2.86	1.08
B-0-7	3.333	55.5	2.72	1.05
B-0-8	0.550	74.5	2.34	1.26

show that the fractionation of sample B-0 was effectively achieved for all samples except fraction 8. It is considered in the fractional solution technique, the higher-molecular-weight fractions are eluted later and have more chance of overlapping of low-molecular-weight fractions, which makes the MWD of later fractions broader. The GPC patterns of the fractions of B-0 in Figure 1 demonstrate these phenomena. It may also be the case in the fractionation of sample B-3. In the fractionation of sample A-4, gelation occurred in the course of recovery of the fraction and this made the MWD of the fractions much broader.

It is noted, however, that osmotic-pressure measurements are subject to a large experimental

Table V. Results of fractionation and osmotic pressure measurements for branched polymers, B-3 and A-4

Sample	W , g	$M_n \times 10^{-4}$	$A_2 \times 10^4$, mol/cc g ²	M_w/M_n
B-3-1	0.985	3.91	8.03	1.38
B-3-2	1.305	7.83	5.70	1.13
B-3-3	1.953	13.0	4.98	0.98
B-3-4	2.425	19.2	4.52	0.91
B-3-5	2.325	27.3	4.75	1.00
B-3-6	2.349	33.9	4.09	1.08
B-3-7	2.133	40.3	3.25	1.15
B-3-8	1.217	44.3	3.16	1.33
B-3-9	3.437	90.8	2.42	1.26
B-3-10	2.375	87.7	2.54	1.65
B-3-11	0.459	113	2.39	1.90
B-3-12	0.250	211	2.23	2.13
A-4-1		74.5	2.53	1.97
A-4-2		191	1.75	2.45
A-4-3		122	2.04	5.73

error in the high-molecular-weight region. Thus the ratios, M_w/M_n , for the fractions with M_n above 800000 involve an error of some degree.

The cumulative MWD curves of B-0 and B-3 are shown in Figures 2 and 3 and are compared with the theoretical curves. The theoretical curves were obtained by plotting $\sum_{x=0}^x W_x$ against x , where x is the relative degree of polymerization and W_x is the weight fraction. W_x was

Figure 1. Gel-permeation chromatograph of B-0 (a) and B-0 fractions (b).

Figure 2. Cumulative molecular weight distribution curve of B-0. The steps indicate the experimental fractions; — indicates the experimental obtained by fractionation; ---- indicates the theoretical distribution with γ and weight-average molecular weight at 0 and 296000; -.-.- indicates the experimental obtained by GPC.

Figure 3. Cumulative molecular weight distribution curve of B-3. The steps indicate the experimental fractions; — indicates the experimental obtained by fractionation; ---- and -.-.- indicate the theoretical distribution with weight-average molecular weight of the primary molecules at 296000 and with γ at 0.50 and 0.60 respectively.

given by eq 3 in Part I and calculated using a high speed computer. The results of calculations are again given in Table VI with $m_0 y_w = 296000$ and $\gamma = 0.5$ and in Table VII with $m_0 y_w = 162000$

and $\gamma = 0.90$, where m_0 , y_w and γ is the monomer molecular weight, the weight-average degree of polymerization of the primary molecules and the branching parameter respectively. In Figure 2,

Table VI. Distribution of molecular weight, W_x , and of branch unit, n_x , calculated from the Stockmayer distribution with a branching parameter, γ , to be 0.50 and weight-average molecular weight of primary molecules, $m_0 y_w$, to be 296000

x	$M(=x m_0 y_w / 2) \times 10^{-4}$	W_x	n_x	$g(n_x)^a$	$h^{-1}(n_x)^b$
0	—	—	—	—	—
0.125	1.85	1.069×10^{-1}	4.069×10^{-5}	—	—
0.250	3.70	1.830×10^{-1}	3.255×10^{-4}	—	—
0.500	7.40	2.683×10^{-1}	2.600×10^{-3}	—	—
1.000	14.80	2.925×10^{-1}	2.058×10^{-2}	—	—
2	29.60	1.925×10^{-1}	1.518×10^{-1}	0.970	1.009
4	59.20	7.342×10^{-2}	7.900×10^{-1}	0.865	1.054
6	88.80	3.672×10^{-2}	1.570	0.758	1.098
8	118.40	2.153×10^{-2}	2.358	0.680	1.135
10	148.00	1.381×10^{-2}	3.148	0.623	1.165
12	177.60	9.387×10^{-3}	3.939	0.580	1.192
14	207.20	6.643×10^{-3}	4.731	0.545	1.217
21	310.80	2.406×10^{-3}	7.506	0.460	1.289
28	414.40	1.035×10^{-3}	10.280	0.407	1.352
56	828.80	6.972×10^{-5}	21.390	0.301	1.525
84	1243	7.199×10^{-6}	32.500	—	—

^a Calculated from the equation $g(n_x) = [(1 + n_x/3)^{1/2} + 4n/3\pi]^{-1/2}$.

^b $h^{-1}(n_x)$ was read from the figure which was obtained by replotting Table II of M. Kurata and M. Fukatsu, *J. Chem. Phys.*, **41**, 2934 (1964).

Table VII. Distribution of molecular weight, W_x , and of branch unit, n_x , calculated from the Stockmayer distribution with a branching parameter, γ , to be 0.90 and weight-average molecular weight of primary molecules $m_0 y_w$, to be 162000

x	$M(=x m_0 y_w / 2) \times 10^{-4}$	W_x	n_x	$g(n_x)$	$h^{-1}(n_x)$
0	—	—	—	—	—
0.125	1.01	1.043×10^{-1}	7.324×10^{-5}	—	—
0.250	2.03	1.741×10^{-1}	5.857×10^{-4}	—	—
0.500	4.05	2.433×10^{-1}	4.674×10^{-3}	—	—
1.000	8.10	2.434×10^{-1}	3.668×10^{-2}	—	—
2	16.20	1.451×10^{-1}	2.557×10^{-1}	0.952	1.020
4	32.40	5.772×10^{-2}	1.125	0.815	1.073
6	48.60	3.218×10^{-2}	2.081	0.704	1.123
8	64.80	2.111×10^{-2}	3.042	0.630	1.161
10	81.00	1.517×10^{-2}	4.004	0.577	1.194
12	97.20	1.156×10^{-2}	4.968	0.536	1.223
14	113.40	9.171×10^{-3}	5.932	0.503	1.250
21	170.10	4.966×10^{-3}	9.309	0.428	1.331
28	226.80	3.197×10^{-3}	12.690	0.377	1.397
56	453.60	1.082×10^{-3}	26.200	0.276	1.580
84	680.40	5.613×10^{-3}	39.720	0.226	1.681

the chain curve is calculated from the GPC diagram using a calibration curve obtained by plotting peak counts of the four fractions of B-0 against the molecular weight, M_w . The agreement of the three curves in Figure 2 is quite satisfactory. The molecular weight distribution of B-0 is, however, somewhat narrower than the theoretical, that is, the "most probable distribution". Discussion of this difference is beyond the scope of this report. The MWD curve obtained by GPC is somewhat broader than others, which may be due to the procedure for treating the GPC data, such as an incomplete calibration curve and the broadening effect in the column. In Figure 3, the MWD of B-3 obtained by the fractionation is compared with the theoretical. As the branching parameter γ of B-3 was determined to be 0.523, the experimental curve must lie between two theoretical curves with $\gamma=0.50$ and $\gamma=0.60$ if the sample had a Stockmayer distribution. It is found that it is true within experimental error.

Thus, it is considered that the randomly branched polydisperse polymers, A-series and B-series, which were prepared by copolymerization

of MMA with EDMA in the previous work are well characterized by the Stockmayer molecular weight distribution.

The root-mean-square radii of gyration obtained by light-scattering measurements were plotted in double logarithmic scale against M_w in Figure 4. For the linear molecules, the following relation is obtained.

$$\langle S_1^2 \rangle_z^{1/2} = 1.198 \times 10^{-2} M_w^{0.76} (\text{\AA}) \quad (1)$$

It is found that among the fractions of B-3, fractions having the molecular weight higher than that of B-3-7 contain branching to a measurable extent. We can now evaluate theoretically the contraction factor g of each molecule which constitutes the whole polymer B-3 and A-4. The number of branch units, n_x , of the molecule having the relative degree of polymerization x is tabulated in Tables VI and VII using the Stockmayer distribution. The value of g is thus obtained from the equation⁵:

$$g(n_x) = \langle S_b^2 \rangle / \langle S_1^2 \rangle = \left[\left(1 + \frac{n_x}{3} \right)^{1/2} + \frac{4n_x}{3\pi} \right]^{-1/2} \quad (2)$$

Figure 4. Log-log plot of root-mean-square radius of gyration against M_w : ○, B-0 fractions; ◐, B-3 fractions; ●, A-4 fractions. The dashed curve indicates the theoretical curve with weight-average molecular weight of the primary molecules at 296000 and γ at 0.50; the broken curve indicates that with M_w of the primary molecules at 162000 and γ at 0.90.

where the subscripts, b and l, represent branched and linear molecules respectively. The results are given in the fifth column of the tables. The quantities $\langle S^2 \rangle$ of eq 2 stand for only the value measured in the theta state. But assuming eq 2 holds for a good solvent, we can estimate $\langle S_b^2 \rangle$ of the molecule having molecular weight $M(=xy_w \cdot m_0/2)$ with the aid of eq 1. The theoretical curves are shown in Figure 4 by the dashed curve for B-3 and by the dotted curve for A-4. The experimental points are in good agreement with the theoretical. It is noted, however, that as the experimental samples have some molecular weight distribution, it is difficult to compare experimental results quantitatively with the theoretical and also to discuss the excluded volume effect of branched molecules.

Figures 5 and 6 show double logarithmic plots of intrinsic viscosity against M_w . The viscosity equations of linear polymer in acetonitrile at 38°C and in methylethylketone at 40°C are obtained:

$$[\eta]_l = 6.50 \times 10^{-4} M_w^{0.48} \quad (3)$$

$$[\eta]_l = 1.24 \times 10^{-4} M_w^{0.67} \quad (4)$$

The exponent of M_w in eq 3 does not become 0.5, but the difference is so small that it may safely be assumed that the intrinsic viscosity in eq 3 stands for the value in the theta state. The dashed and the broken curves are the theoretical which are obtained from eq 5 derived by Zimm and Kilb and using the value of g given in the Tables VI and VII.

$$[\eta]_b = g^{1/2} [\eta]_l \quad (5)$$

The agreement with experimental points is quite satisfactory in the theta state, but in good solvents the experimental points deviate downward from the theoretical in the high-molecular-weight region. Though the discrepancy between the experimental points and theoretical curves in Figure 6 diminishes by taking the exponent of g in eq 5 greater than 1/2, this deviation from the $g^{1/2}$ -rule may be due to the difference in excluded volume effect between a branched and a linear molecule, for in the theta state the $g^{1/2}$ rule is quite valid. It is well known that the intrinsic viscosity in a good solvent is written in the form:

$$[\eta] = [\eta]_\theta (\alpha_\eta)^3 \quad (6)$$

Figure 5. Log-log plot of intrinsic viscosity against M_w in acetonitrile at 38°C. Symbols and curved lines are the same as in Figure 4.

Figure 6. Log-log plot of intrinsic viscosity against M_w in MEK at 40°C. The chain curve indicates the theoretical with weight-average molecular weight of the primary molecules at 162000 and γ as 0.90, using the relation $[\eta]_b = [\eta]_l \gamma^{3/2}$. Other symbols and curved lines are the same as in Figure 4.

Figure 7. Log-log plot of cubic of expansion factor, $(\alpha\eta)_l^3$, of a linear polymer against that of a branched polymer, $(\alpha\eta)_b^3$. Symbols are the same as in Figure 4.

Figure 8. Relation between ratio $(\alpha_{\eta})_1^3/(\alpha_{\eta})_b^3$ and number of branch units. Symbols are the same as in Figure 4.

where $[\eta]_{\theta}$ is the intrinsic viscosity in the theta state and α_{η} is the expansion factor. We can evaluate the expansion factor of a branched molecule, $(\alpha_{\eta})_b$, and that of a linear molecule, $(\alpha_{\eta})_1$, having the same molecular weight. Figure 7 shows these values in double logarithmic plots. One finds that in the region of large α_{η} , $(\alpha_{\eta})_1^3$ is greater than $(\alpha_{\eta})_b^3$. This is in accord with the results of Abe and coworkers obtained for randomly branched polystyrene. Our result contradicts the prediction of Berry and Orfino⁶ that a star-type branched molecule expands somewhat greater than a linear molecule. In order to ascertain the difference between $(\alpha_{\eta})_b$ and $(\alpha_{\eta})_1$ more clearly, the ratios $(\alpha_{\eta})_1^3/(\alpha_{\eta})_b^3$ are plotted against the number of branch units, n , of the sample in Figure 8. It is found that the ratio increases monotonously with n in both series A and B. In the case of the star-type molecule having three branches, however, it was reported⁷ $(\alpha_{\eta})_b$ was nearly equal to $(\alpha_{\eta})_1^3$. From Figure 8, it is considered that in the range of small n (less than about five), the difference between $(\alpha_{\eta})_b^3$ and $(\alpha_{\eta})_1^3$ is so small that it cannot be detected experimentally. Thus it is concluded that $(\alpha_{\eta})_b$ is somewhat smaller than $(\alpha_{\eta})_1$ and the difference is perhaps a function of the number of branch units and this is the reason why the intrinsic viscosity in a good solvent

deviates from the $g^{1/2}$ -rule in the range of large numbers of branch units. The excluded volume effect of a branched molecule, however, must be further investigated both theoretically and experimentally.

The values of g experimentally determined with the aid of eq 3 and 5 are summarized in Table VIII. The average number of branch units, n_x obtained by eq 2 are also given in the fifth

Table VIII. Number of branch units of fractionated samples obtained experimentally

Sample	$[\eta]_b$	$[\eta]_1^a$	g^b	$\bar{n}_x^c$	$\lambda \times 10^{-4d}$
B-3-7	0.314	0.327	0.920	0.440	106
B-3-8	0.337	0.365	0.851	0.880	67.0
B-3-9	0.412	0.500	0.680	2.360	48.4
B-3-10	0.435	0.558	0.609	3.370	43.0
B-3-11	0.456	0.671	0.462	7.450	28.9
B-3-12	0.612	0.956	0.410	10.100	44.4
A-4-1	0.361	0.562	0.413	10.000	14.7
A-4-2	0.478	0.972	0.242	34.100	14.7
A-4-3	0.574	1.180	0.237	36.000	19.4

^a Calculated from $[\eta]_1 = 6.50 \times 10^{-4} M^{0.48}$ which was obtained from B-0 fractions.

^b Deduced from $[\eta]_b/[\eta]_1 = g^{1/2}$.

^c Calculated from the equation $g = [(1 + n_x/6)^{1/2} + 4n_x/3\pi]^{-1/2}$.

^d $\lambda = M_w/n_x$.

column and the average molecular weight per branch unit, $\lambda (=M_w/n_x)$, in the sixth column. The weight-average number of branch units, $n_w (= \sum W_x n_x / \sum W_x)$, for the whole polymer B-3 is then found by averaging n_x to be 1.13; the branching parameter, $\gamma (=n_w/(1+n_w))$, is now found to be 0.532, which is much closer to the value obtained in the previous work (Table I). The average molecular weight per branch unit is nearly constant within a series except the fraction having a small branch unit, which indicate the samples are randomly branched molecules.

The results of sedimentation velocity measurements are given in Table IX. For the samples from B-0-1 to B-0-5, the MWD was sharp enough to determine the sedimentation constant, S , by the movement of the peak position in the Schlieren diagrams. Five solutions of different concentrations ranging about from 0.2 g/dl to 0.6 g/dl were run for each sample and the extrapolation to infinite dilution was performed by the following equation

$$S_c^0 = S_0^0(1 - k_s c) \quad (7)$$

where S_0^0 is a sedimentation constant of infinite dilution at 1 atom, c is an initial concentration and k_s is a parameter representing the concentration dependence. As for the sample mentioned above measurements were carried out in the vicinity of the meniscus, sedimenta-

tion constant at concentration c , S_c , being nearly equal to the quantity measured at 1 atom, S_c^0 . Thus S_c was used instead of S_c^0 in eq 7. For other samples, the Schlieren diagrams were not symmetrical, but rather *skew* and broad; $\bar{x}$ given by eq 8 was used instead of the peak position.⁸

$$\bar{x}^2 = \int_{x_0}^{x_p} x^2 \frac{\partial c}{\partial x} dx / \int_{x_0}^{x_p} \frac{\partial c}{\partial x} dx \quad (8)$$

where x_0 and x_p are respectively the distance from the center of a rotor to the meniscus and to the plateau region. In calculating eq 8, it is necessary to measure the complete Schlieren diagrams. In the case of the higher-molecular-weight region of Schlieren diagram sediments near the bottom of the cell, it is necessary to perform a pressure correction. This was done by the following equation according to Fujita.⁹

$$\ln(\bar{x}/x_0)/\omega^2 t = S_c^0 \{1 + K[(\bar{x}/x_0)^2 - 1]\} \quad (9)$$

$$K = -m/2 + (1-m)/2 \cdot k_s c \quad (10)$$

$$m = \frac{1}{2} \mu \omega^2 \rho_0^0 x_0^2 \quad (11)$$

where ω is the rotor speed, t is the time which is required for sedimentation, μ is a parameter of the pressure dependence and ρ_0^0 is density of the solvent. The extrapolation to infinite dilution was carried out by substituting S_c^0 obtained by eq 9 into 7.

For example, Figures 9 and 10 show some of

Figure 9. $\ln(\bar{x}/x_0)/\omega^2 t$ vs. $(\bar{x}/x_0)^2 - 1$ plots for B-0-7.

these extrapolations. It is noted that the sedimentation constant of this system (PMMA—acetonitrile) shows a high value and its pressure dependence is also high in spite of a rather slow rotor speed. For example, from Figure

9 we can estimate the value of μ with the aid of eq 10 and 11, obtaining a value of about 7×10^{-9} . This value is much larger than the system of polystyrene—cyclohexane¹⁰ ($\mu = 1 \times 10^{-9} - 2 \times 10^{-9}$). S_0^0 obtained by the above pro-

Figure 10. S_c^0 vs. concentration for some fractions.

Figure 11. Log-log plot of sedimentation constant obtained in acetonitrile at 38°C against M_w . Symbols and curved lines are the same as in Figure 4.

cedure, then, is plotted in double logarithmic form against M_w in Figure 11. For a linear molecule the following equation is established:

$$S_0^0 = 0.186 \times M^{0.510} \quad (12)$$

In Figure 11 are also shown the theoretical curves calculated by the relation:

$$S_b = h^{-1}(n) S_l \quad (13)$$

where S_b and S_l are sedimentation constants of branched and a linear molecule having the same molecular weight. $h^{-1}(n)$, the inverse of the ratio of the Stokes radius of a branched molecule to that of a linear one, was obtained from Table II of Kurata and Fukatsu.¹¹ The value of $h^{-1}(n)$ for sample B-3 and A-4 are given in the sixth column of Tables VI and VII respectively. The experimental points of branched molecules with narrow MWD are in close agreement with the theoretical, but those of samples with relatively broad MWD show a downward deviation and rather come on the line of linear molecules. This phenomena can be interpreted by means of the previous calculation of the sedimentation constant of a polydisperse randomly branched polymer. Thus it may be concluded that a randomly branched molecule with narrow MWD sediments by the factor h^{-1} faster than a linear molecule, at least in the theta state. Now according to Flory and Mandelkern,¹² a sedimentation constant is written in the form of eq 14 in relation to the intrinsic viscosity.

$$S[\eta]^{1/3} M^{-3/2} = \Phi_0^{1/3} P_0^{-1} (1 - \bar{v}\rho) / \eta_0 N_A \quad (14)$$

where Φ_0 and P_0 are constants, $\bar{v}$ is a partial specific volume of a polymer, ρ is a density of the solution, η_0 is a viscosity of the solvent and N_A is the Avogadro number. In acetonitrile at 38°C, $\bar{v}$ is determined to be 0.763, and the value of $\Phi_0^{1/3} P_0^{-1}$ is calculated by eq 14. The values are also given in Table IX with the molecular weight and the intrinsic viscosity. For the linear polymer, these values are nearly constant giving 2.14×10^{-6} on average. The average value is smaller than the usual value 2.5×10^{-6} which is often obtained in good solvents.

It is generally admitted that the value of $\Phi_0^{1/3} P_0^{-1}$ is not the universal constant, but varies

Table IX. Results of sedimentation velocity measurements and $\Phi^{1/3} \times P^{-1}$

Sample	$S_0^0(S)$	$M \times 10^{-4}$	$[\eta]$, dl/g	$\Phi^{1/3} P^{-1} \times 10^{-6}$
B-0-1	13.6	4.59	0.110	2.27
B-0-2	17.5	8.19	0.163	2.24
B-0-3	21.1	12.60	0.172	2.09
B-0-4	25.6	18.00	0.210	2.13
B-0-5	31.2	26.10	0.242	2.13
B-0-6	37.1	38.80	0.301	2.09
B-0-7	47.1	58.50	0.365	2.15
B-0-8	57.3	94.00	0.441	2.00
				av 2.14
B-3-7	44.0	46.50	0.314	2.23
B-3-8	49.6	59.00	0.337	2.19
B-3-9	69.5	114	0.412	2.12
B-3-10	81.1	145	0.435	2.14
B-3-11	87.0	215	0.456	1.80
B-3-12	157.7	449	0.612	2.20
A-4-1	78.0	147	0.361	1.92
A-4-2	136.5	468	0.478	1.70
A-4-3	165.5	699	0.574	1.68

from solvent to solvent. For a branched molecule, the value is nearly constant from samples B-3-7 to B-3-10 and equal to that of a linear molecule, but decreases gradually to 1.68×10^{-6} . That is, for a branched molecule with narrow MWD:

$$\Phi_{0,b}^{1/3} P_{0,b}^{-1} = \Phi_{0,l}^{1/3} P_{0,l}^{-1} \quad (15)$$

where the subscripts b and l represent a branched and a linear molecule respectively. As it is considered that $\bar{v}$ is the same for a branched and a linear molecule, we obtain from eq 14 and 15 with the aid of the relation $[\eta]_b = g^{1/2} [\eta]_l$:

$$S_b = g^{-1/6} S_l \quad (16)$$

That is:

$$S_b / S_l = h^{-1} = g^{-1/6} \quad (17)$$

Since an intrinsic viscosity is proportional, in the nondraining limit, to the effective hydrodynamic volume, the ratio of the effective hydrodynamic radius of a branched molecule to that of a linear one is given as

$$h_\eta = ([\eta]_b / [\eta]_l)^{1/3} = g^{1/6} \quad (18)$$

Thus comparison of h with h_η shows that the sensitivity of the hydrodynamic radius to the branching is nearly the same in the intrinsic

viscosity as in the friction constant for a randomly branched molecule. The intrinsic viscosity, however, is proportional to h_η^3 and is accordingly more sensitive to the branching than the sedimentation coefficient which is proportional to h^{-1} .

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