*Studies of Polybutene. II. On the Molecular Weight Distribution and the Solution Properties**

By Ryūichi ENDŌ, Kazuyoshi IIMURA and Masatami TAKEDA

(Received February 1, 1964)

Various commercial polybutenes have been obtained from several sources. Infrared study makes it seem that the polybutene is almost identical with a low-molecular-weight polyisobutylene.¹⁾ Far fewer studies of the solution properties of the polymers with molecular weights ranging from 1000 to 10000 were carried out than on the usual high polymers, although recently the vapor pressure osmometer has become available for these low-molecular-weight polymers. Previous investigation of the polybutene has only dealt with its rheological property,²⁾ not with its solution property because of its extremely low molecular weight.

The present investigation has been undertaken to study the molecular weight and the molecular weight distribution of polybutene. Furthermore, according to the theory of Stockmayer and Fixman,³⁾ the unperturbed dimension of the polybutene fractions has been calculated from the relationship between the intrinsic viscosity and the molecular weight, and compared with the data reported by Fox and Flory⁴⁾ on low-molecular-weight polyisobutylene.

Experimental

Samples.—All the polybutenes employed were commercial products: Indopol of Amoco, Oronite of California Chemicals, and Polyvis of Cosden. All these samples except Indopol L-10 appeared as transparant viscous liquids.

The solvent and non-solvent were purified in the usual ways.⁵⁾

Fractionation. — Fractional extraction has been applied with benzene as a solvent and methanol as a non-solvent. The fractionation was carried out using benzene-methanol mixtures, initially with a mixture rich in the non-solvent and finally with a mixture rich in the solvent, at room temperature. Then, the lowest-molecular-weight fraction was extracted from the sample. All the sample were divided into about eight or nine fractions.

Viscosity Measurement.—Samples were dissolved into benzene at room temperatures. The viscosities were measured with dilution in an Ubbelohde-type

---

* Presented at the 12th Annual Meeting of the Society of Polymer Science, of Japan, Tokyo, May, 1963.

1) K. Iimura, R. Endō and M. Takeda, This Bulletin, 37, 874 (1964).

2) H. Leaderman, R. G. Smith and R. W. Jones, *J. Polymer Sci.*, **14**, 47 (1954).

3) W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, Part C, No. 1, 137 (1963).

4) T. G. Fox and P. J. Flory, *J. Phys. and Colloid Chem.*, **53**, 197 (1949).

5) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," Interscience Publishers, N. Y. (1955).

viscometer at 30°C. The temperature of the double water bath, in which the viscometer was mounted vertically by using a specially-designed clamp, was maintained constant within ±0.005°C. Intrinsic viscosities were treated by the Huggins relation, and the data were calculated by the least-square method.

Molecular Weight Measurement.—The molecular weight of unfractionated samples was determined by the cryoscopic method in benzene. The molecular chain of polybutene is known to be a linear chain with one double bond at the end of the chain.[6]

Therefore, it is possible to determine the molecular weight of the same samples by the end-group analysis. The number of double bonds was determined using a modified Hübler method[7] in the following manner: about 1 g. of a sample was dissolved into 20 ml. of chloroform in a 500 ml. Erlenmeyer flask and added to a definite volume of an iodine solution ($I_2+Hg_2Cl_2$ in alcohol). The flask was then shaken frequently by hand. The reaction to the double bond with iodine was carried out in a dark oven at 30°C; the reaction mixture was kept there for 48 hr. (e. g., see Fig. 3). The molecular weight was calculated from the following equation (1);

$$\overline{M}_n=1/[I_2] \qquad (1)$$

The observed values agreed closely with that determined by the cryoscopic method. Since the amount of each fraction was limited, the molecular weight was determined mainly by the end-group analysis method.

Results and Discussion

Fractionation and Intrinsic Viscosity.—The solubility in a benzene-methanol mixed solvent was determined for Indopol L-10 as the lower, the Indopol H-35 as the medium, and for Indopol H-300 as the higher molecular weight sample respectively. The results are shown in Fig. 1. Figure 1 shows that the fractionation can be carried out with the mixed solvents by varying the volume fraction of benzene. Because these polymers have lower molecular weights, it seems likely that the fractionation is effected only by the difference in the dissolution energy of polymer molecules in mixed solvents and not by the entropy effect as in the usual high polymers. According to Brönsted's law of partition,[8] there exists a relation:

$$N_1/N_2=\exp(-ME/RT) \qquad (2)$$

where N_1 is the concentration of polymers in the solution phase, N_2 is the concentration of polymers in the gel phase, M is the molecular weight of dissolved polymers, and E is the dissolution energy of a monomer unit of polybutene. If the dissolution energy of some mixed solvent is a constant, the value of N_1/N_2 becomes smaller for the larger M. Generally, the value of N_1/N_2 increases with an increase in the dissolution energy or with the larger volume fraction of benzene in the mixed solvent. If the fractionation follows Eq. 2, a linear relation may be obtained between $\ln N_1/N_2$ and the dissolution energy, E, of mixed solvents.

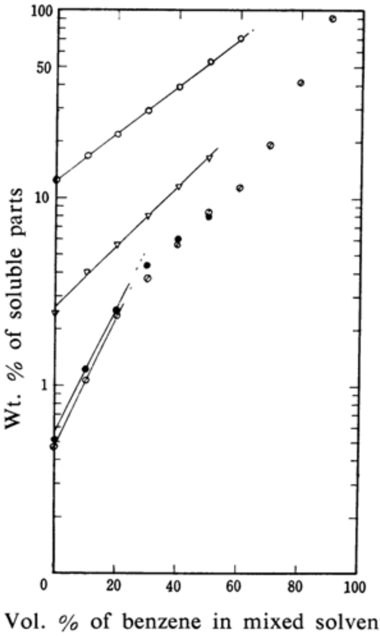

Fig. 1. Relation between the volume fraction of benzene in benzene-methanol mixed solvent and the weight fraction of soluble part.
○ L-10, ▽ H35, ⊘ H300, ● 32

For Indopol L-10, which is of the lowest molecular weight, a linear relation was obtained, but not for Indopol H-35 and Indopol H-300. A more general theory[9] it necessary for treating these samples. The fractions obtained from each sample are given in Table I(a)—(f). The reduced viscosities are plotted against the concentration for Indopol H-300 and Polyvis 3 in Fig. 2(a)—(b). It may be seen from Fig. 2 that the Huggins' relation holds for these samples up to higher concentrations, but for higher-molecular-weight polymers, the nonlinear relation[10] appears in the range of higher concentrations. The intrinsic viscosities of unfractionated samples are shown in Table II.

---

[6] C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley & Sons, Inc., New York (1959), p. 560.

[7] J. Arima, "Analytical Methods of Organic Compounds" (in Japanese), Iwanami, Tokyo, p. 190.

[8] Brönsted, *Z. phys. Chem.*, Bodenstein Festband 257 (1931).

[9] P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y. (1953).

[10] M. Nakamuta, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), 77, 702, 705, 858, 861 (1956).

TABLE I. INTRINSIC VISCOSITIES AND MOLECULAR WEIGHTS OF THE FRACTIONS OF POLYBUTENES

(a) INDOPOL L-10

Fraction No.	Weight	Weight-fraction	$[\eta]$	$\overline{M}_{end}$	$\overline{M}_v$
F-1	1.173_5	12.4_4	0.011_3	240	230
F-2	1.521_7	16.1_3	0.011_5	270	230
F-3	2.303_3	24.4_1	0.012_6	350	260
F-4	2.004_4	21.2_4	0.013_5	350	290
F-5	0.974_1	10.3_2	0.018_0	(330)	430
F-6	0.293_8	3.1_1	0.023_6	390	630
F-7	0.214_9	2.2_8	0.033_8	600	1040
F-8	0.949_8	10.0_7	0.065_3	—	2580

(b) INDOPOL H-35

Fraction No.	Weight	Weight-fraction	$[\eta]$	$\overline{M}_{end}$	$\overline{M}_v$
F-1	1.899_4	19.0_8	0.015_8	380	360
F-2	1.575_5	15.8_3	0.018_3	370	440
F-3	1.331_4	13.3_7	0.023_4	480	620
F-4	1.194_7	12.0_0	0.026_4	830	740
F-5	0.992_8	9.9_7	0.037_3	1460	1190
F-6	0.800_0	8.0_4	0.044_2	—	1500
F-7	0.670_4	6.7_3	0.051_8	(5560)	1870
F-8	1.490_9	14.9_8	0.076_1	—	3190

(c) INDOPOL H-300

Fraction No.	Weight	Weight-fraction	$[\eta]$	$\overline{M}_{end}$	$\overline{M}_v$
F-1	0.676_7	6.6_7	0.019_1	460	470
F-2	1.553_1	15.3_1	0.024_0	600	650
F-3	2.022_9	19.9_4	0.032_3	990	970
F-4	1.980_7	19.5_2	0.040_7	1400	1340
F-5	1.219_1	12.0_2	0.047_3	2070	1650
F-6	1.107_8	10.9_2	0.061_2	3800	2360
F-7	0.745_0	7.3_4	0.076_7	4330	3220
F-8	0.390_1	3.8_5	0.084_2	—	3670
F-9	0.449_2	4.4_3	0.125_4	—	6370

(d) POLYVIS 3

Fraction No.	Weight	Weight-fraction	$[\eta]$	$\overline{M}_{end}$	$\overline{M}_v$
F-1	1.906_8	19.2_8	0.016_8	360	390
F-2	1.797_3	18.1_7	0.019_6	420	490
F-3	1.635_8	16.5_4	0.025_0	510	680
F-4	1.441_8	14.5_8	0.029_3	730	850
F-5	1.115_6	11.2_8	0.036_8	1630	1170
F-6	0.864_3	8.7_4	0.046_5	—	1610
F-7	0.643_8	6.5_1	0.053_5	—	1960
F-8	0.484_7	4.9_0	0.070_7	—	2880

(e) POLYVIS 30

Fraction No.	Weight	Weight-fraction	$[\eta]$	M_{end}	$\overline{M}_v$
F-1	0.647_9	6.3_6	0.014_8	420	330
F-2	1.237_0	12.2_5	0.023_6	710	630
F-3	1.614_0	15.8_5	0.031_8	860	950
F-4	1.766_0	17.3_5	0.040_0	1360	1310
F-5	1.370_0	13.4_6	0.046_9	2250	1630
F-6	1.462_8	14.3_7	0.058_9	2920	2240
F-7	1.266_3	12.4_4	0.073_6	3800	3040
F-8	0.513_6	5.0_5	0.086_6	—	3810
F-9	0.302_4	2.9_7	0.115_1	—	5650

(f) ORONITE 32

Fraction No.	Weight	Weight-fraction	$[\eta]$	$\overline{M}_{end}$	$\overline{M}_v$
F-1	0.685_1	6.8_3	0.017_4	430	410
F-2	1.344_9	13.4_1	0.023_4	710	620
F-3	1.725_3	17.2_0	0.031_6	890	940
F-4	1.952_6	19.4_0	0.040_5	1310	1330
F-5	1.390_6	13.8_6	0.047_4	2280	1660
F-6	1.178_7	11.7_5	0.061_5	2870	2370
F-7	0.897_6	8.9_5	0.072_7	3520	2990
F 8	0.494_4	4.9_3	0.090_3	4980	4040
F-9	0.363_0	3.6_2	0.125_9		6400

Molecular Weight.—The molecular weight of unfractionated samples was determined by means of the cryoscopic method and are listed as $\overline{M}_{cry}$ in Table II. Figure 3 shows the plots of the iodine concentration against the reaction time. Therefore, the molecular weights with an end-group titration $\overline{M}_{end}$ were determined after 48 hr.; they are shown in Table I(a)—(f), and Table II. The agreement of $\overline{M}_{end}$ and $\overline{M}_{cry}$ is fair. Therefore, it has been proved that the molecular chain of polybutene has only one double bond in each chain.

Therefore, the molecular weight determination of fractions has been carried out mainly by end-group analysis, because it requires a smaller amount of sample than does the cryoscopic method.

TABLE II. VISCOSITIES AND MOLECULAR WEIGHTS OF UNFRACTIONATED SAMPLES

Sample	$[\eta]$	M_{end}	$\overline{M}_{cry}$
Indopol L-10	0.019_6	310	310
Indopol H-35	0.034_6	640	630
Indopol H-300	0.051_6	1100	1090
Polyvis 3	0.030_2	660	650
Polyvis 30	0.061_9	1150	1300
Oronite 32	0.052_6	1030	1240

The Relationship between Intrinsic Viscosity and Molecular Weight.—The intrinsic viscosity of fractions is plotted against the molecular weight in Fig. 4. The Mark-Houwink equation was determined by the least squares method to be:

$$[\eta]=2.24\times10^{-4}\overline{M}_n^{0.72_2} \tag{3}$$

On the other hand, Fox and Flory[4] obtained for polyisobutylene with molecular weights from 1000 to 1300000:

$$[\eta]=6.1\times10^{-4}\overline{M}^{0.56} \tag{4}$$

For comparison, a dotted line expressing Flory's equation (4) is also drawn in Fig. 4. The value of the exponent in Eq. 3 is larger than that in Flory's equation (4). Since it is known that the system of polyisobutylene

Table III. Molecular weights of polybutenes

Sample	$\overline{M}_{end}$ a)	$\overline{M}_{cry}$ b)	$\overline{M}_w$ c)	$\overline{M}_n$ c)	$\overline{M}_w/\overline{M}_n$	$\mu_2\times10^{-4}$
Indopol L-10	310	310	280	260	1.08	0.54
Indopol H-35	640	630	1260	750	1.008	38.25
Indopol H-300	1100	1010	1590	1040	1.53	57.32
Polyvis 3	660	650	990	650	1.52	21.97
Polyvis 30	1150	1300	1780	940	1.89	78.64
Oronite 32	1030	1240	1680	990	1.70	68.61

a) Determined by the end-group analysis.
b) Determined by the cryoscopic method.
c) Calculated from the molecular weight distribution.

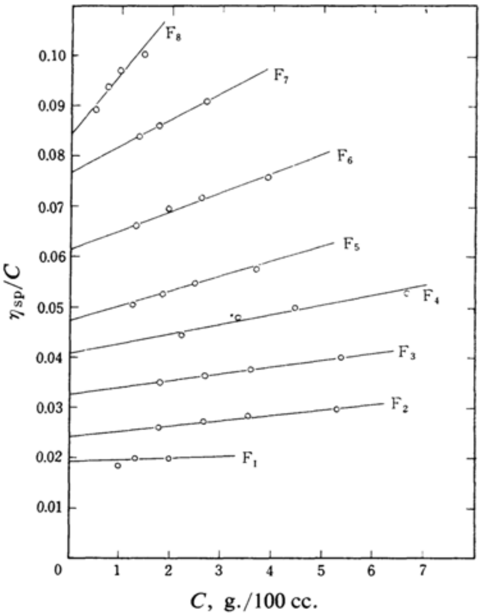

Fig. 2(a). Relation between the reduced viscosity and the concentration of Indopol H-300, at 30°C.

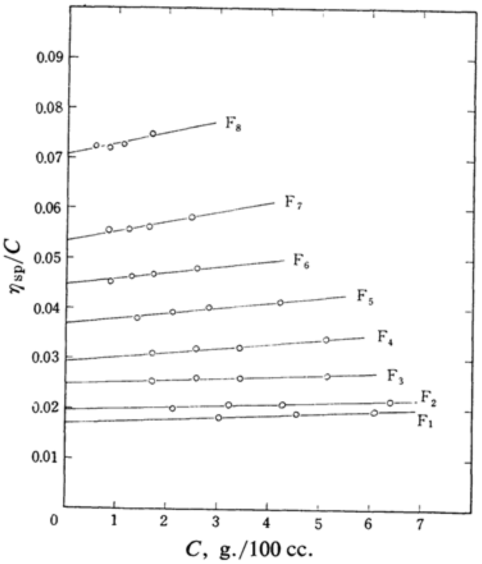

Fig. 2(b). Relation between the reduced viscosity and the concentration of Polyvis 3, at 30°C.

in benzene has the theta temperature at 25°C,[11] the obtained α for polybutene seems to be large. In polymerization, the branching of the polymer chain may occur mainly at the molecule with a higher molecular weight. Because the polyisobutylene has a higher molecular weight than polybutene, it seems that the branching exists in the molecular chain. Since polybutene seems to consist of linear chain molecules with molecular weights ranging from 240 to 7000, the value of the α of polybutene is thought to become larger than that of polyisobutylene.

Recently, Stockmayer and Fixman[3] have demonstrated a means to estimate the unperturbed dimension factor K from the intrinsic viscosity $[\eta]$ by means of the following equation:

$$[\eta]=KM^{1/2}\alpha_\eta{}^3 \tag{5}$$

$$[\eta]=KM^{1/2}+0.51\Phi_0BM \tag{6}$$

$$K=\Phi_0A^3 \tag{7}$$

$$A^2=\langle\overline{L^2}\rangle_0/M \tag{8}$$

where Φ_0 is the universal viscosity constant for chain polymers in theta solvents, B is the polymer-solvent interaction parameter, α_η is the viscosity expansion factor,[12] and $\langle\overline{L^2}\rangle_0$ is the mean square unperturbed end-to-end distance. Equation 6 gives the unperturbed molecular dimension, A^2, from the measured value of K without using the theta solvent. If the plots of $[\eta]M^{-1/2}$ against $M^{1/2}$ are extrapolated to zero molecular weight, we have the value of K. Experimental results are shown in Fig. 5. The value of K obtained

---

[11] T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.*, 73, 1909 (1951).

[12] M. Kurata and W. H. Stockmayer, *Progress Polymer Phys. Japan*, 5, 23 (1962).

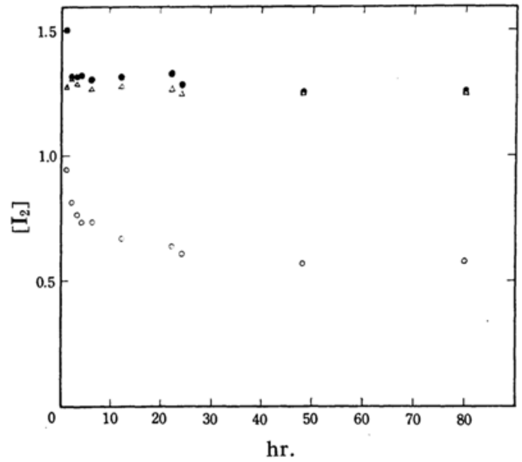

Fig. 3. Change of iodine value with time. The open circle and triangle are the Indopol L-10 and Polyvis 30 respectively. The closed circle is blank test.

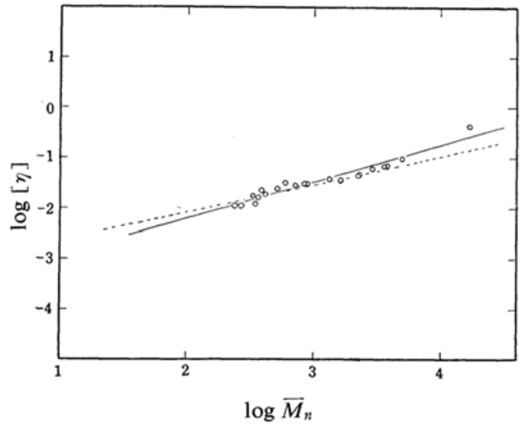

Fig. 4. Relation between the intrinsic viscosity and the molecular weight. Dotted line shows Flory's result.

in the theta solvent is given⁹⁾ as 10.6×10^{-4}, as is shown on the ordinate axis by an arrow in Fig. 5. Although the experimental points are scattered widely, the value of K obtained from the present work shows a tendency to be smaller than 10.6×10^{-4}. This effect seems to arise from the end-effect of the molecular chain of polybutene because of its smaller molecular weight.¹³⁾

Molecular Weight Distribution. — The end-group analysis is less reliable for the determination of the molecular weight of higher fractions. The molecular weight of all fractions was re-calculated by using Eq. 3 and is shown as $\overline{M}_v$ in Table I (a)—(f).

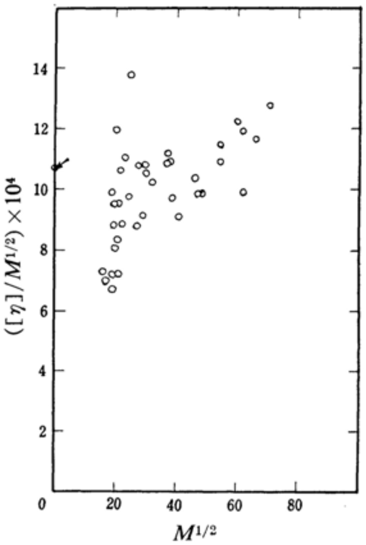

Fig. 5. Relation between $[\eta]M^{-1/2}$ and $M^{1/2}$. The arrow shows the value of K obtained in θ-solvent.

Integral distribution curves are expressed as plots of the cumulative weight fraction against the molecular weight. The cumulative weight fraction corresponding to the molecular weight, M_i, of the i-th fraction, designated as W_i, is expressed by the following equation;

$$W_i = w_i/2 + \sum_{j=1}^{i-1} w_j \tag{9}$$

where w_i and w_j are the weight fractions of the i-th and j-th fractions respectively. The integral distribution curves are then converted into the differential distribution curves (cf. Fig. 6 (a)—(f)). The number-average molecular weight $\overline{M}_n$, the weight-average molecular weight $\overline{M}_w$, the $\overline{M}_w/\overline{M}_n$ ratio and a variance, μ_2, were also calculated¹⁴⁾ for these distributions; they are shown in Table III. The calculated values of the number-average molecular weight, with the exception of Indopol L-10, are essentially identical with the observed values. The values of $\overline{M}_w/\overline{M}_n$, also with the exception of Indopol L-10, are equal to those of high polymers in general. Therefore, it is found that such a low-molecular-weight polymer keeps the inhomogeneity of molecular weight.

We have tried to fit Schulz's molecular weight distribution function¹⁵⁾ to our experimental results. This function is:

$$f(M) = M \ln^2 a a^M \tag{10}$$

where M is the molecular weight and a is the probability of propagation for the active

---

13) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolym.-Forsch.*, **3**, 196 (1963).

14) R. Endō *Chem. High Polymers Japan* (*Kōbunshi Kagaku*), **18**, 214 (1961).

15) G. V. Schulz, *Z. phys. Chem.*, **B30**, 379 (1935).

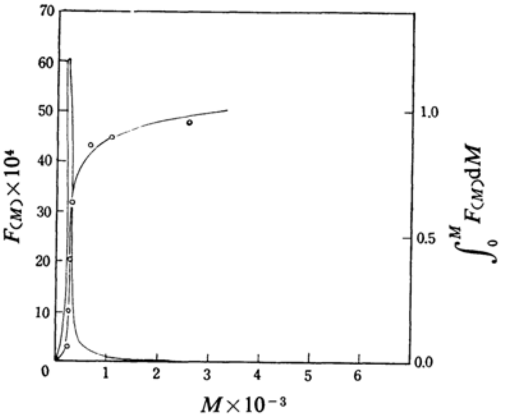

Fig. 6(a). Molecular weight distribution curve of Indopol L-10.

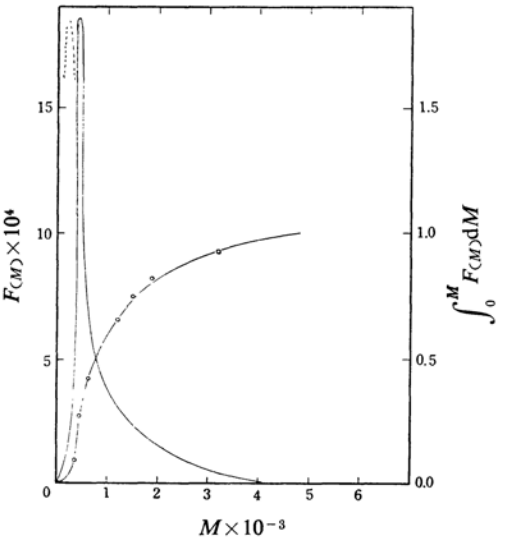

Fig. 6(b). Molecular weight distribution curve of Indopol H-35. Dotted curve was calculated from Schulz's function.

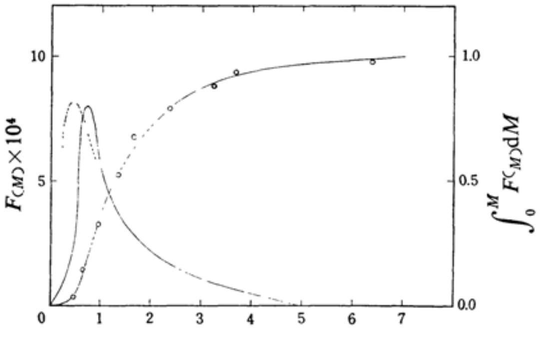

Fig. 6(c). Molecular weight distribution curve of Indopol H-300. Dotted curve was calculated from Schulz's function.

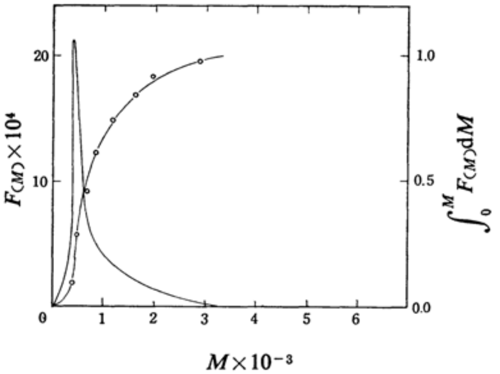

Fig. 6(d). Molecular weight distribution curve of Polyvis 3.

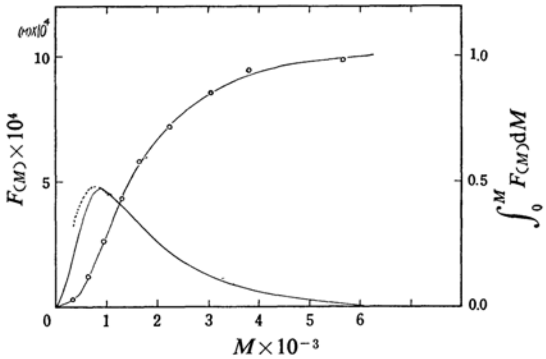

Fig. 6(e). Molecular weight distribution curve of Polyvis 30. Dotted curve was calculated from Schulz's function.

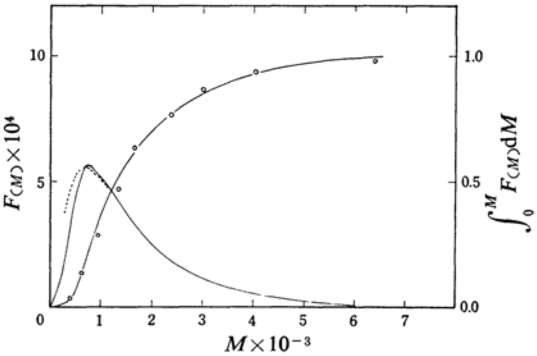

Fig. 6(f). Molecular weight distribution curve of Oronite 32. Dotted curve was calculated from Schulz's function.

TABLE IV. THE VALUES OF a AND χ

Sample	a	χ*	Ref.
Indopol H-35	(0.9950)	(0.0050)	This work
Indopol H-300	(0.9978)	(0.0022)	This work
Polyvis 30	0.9987	0.0013	This work
Oronite 32	0.9985	0.0015	This work
Polyisobutylene	0.9982	0.0018	17

* $1-\chi=a$ where $\chi \ll 1$.

molecule in polymerization. The parameters a in Eq. 10 were calculated from the observed distribution function; they are listed in Table IV. For comparison, theoretical curves expressing Eq. 10 are also given as dotted lines in Figs. 6(b), 6(c), 6(e) and 6(f). Some difference between the theoretical and the observed curves may be seen in Fig. 6(b). The theoretical curves are not drawn in Figs. 6(a) and 6(d) because the observed curves are not in good agreement with the theoretical ones. These disagreements are thought to be caused by their smaller molecular weights. Though the Indopol H-300 shown in Fig. 6(c) is of a higher molecular weight than the other three samples, the agreement between the observed curve and the theoretical one for it is not very good. In general, it is felt that the observed curves for the samples of Indopol series do not agree with the theoretical curves. On the other hand, the curves for the other samples shown in Figs. 6(e) and 6(f) are in close agreement with theoretical ones.

The ratio of the probability of termination to the probability of propagation, χ, is then calculated from the value of a; it is also shown in Table IV. For comparison, the value of a for polyisobutylene[16] is also listed in Table IV. Because the material gas of polybutene consists of mixed olefin with carbon numbers from two to six, it seems difficult to compare the mechanism of its polymerization directly with that of polyisobutylene. However, as the values of a are nearly equal to that of polyisobutylene, it may suggest that the polymerization mechanism of polybutene is similar to that of polyisobutylene.

The authors are indebted to Miss Kazumi Nakamura for her assistance.

Tokyo College of Science
Department of Chemistry
Faculty of Science
Kagurazaka, Shinjuku-ku
Tokyo

---

[16] M. Imoto, "*Chemistry of Synthetic High Polymers*" (in Japanese), Sōgensha, Tokyo (1950), p. 84.