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Studies of Poly-2-vinylpyridine. I. Suspension Polymerization and Molecular Weight Distribution

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2-Vinylpyridine has been polymerized by the suspension method. A stable suspension has been obtained using a mixture of sodium butylnaphthalene sulfonate and gelatine as a stabilizer in the concentration ranges of 0.025—0.75 per cent (for the former) and 0.75—1.0 per cent (for the latter) in water. The molecular weight of polymers thus obtained from this stable suspension system could be controlled by varying the concentration of azo-bis-isobutyronitrile and the temperature. The M_w/M_n ratios of the polymers obtained by the above method are relatively large; from 3.5 to 5. Precipitation fractionation has been carried out for a polymer obtained using ethyl methyl ketone as a solvent and ligroin as a precipitant at a constant temperature. Three kinds of molecular weight distribution curves have been obtained by applying the data of fractionation to (1) Tung's method, (2) exponential-type and (3) logarithmic normal-type molecular weight distribution functions. By comparing the average molecular weights, M_w and M_n calculated from each curve with the experimental values, it was found that the molecular weight distribution of the fraction can be well represented by the function 2 or 3.

Various copolymers[1-4] of 2-vinylpyridine have been extensively studied because of their practical importance. The derivatives of poly-2-vinylpyridine have also fully been investigated from the point of view of polyelectrolytes[5-8] and

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[1] W. W. Rinne and J. E. Rose, *Ind. Eng. Chem.*, **40**, 1437 (1948).

[2] S. Yuguchi and M. Watanabe, *Kobunshi Kagaku*, **17**, 465 (1960).

[3] K. Mizutani and S. Suzuki, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **64**, 577 (1961).

[4] T. Ida, S. Kishi, S. Takahashi and I. Utsumi, *J. Pharm. Sci.*, **51**, 1061 (1962).

[5] W. N. Maclay and R. M. Fuoss, *J. Polymer Sci.*, **6**, 511 (1951).

[6] H. L. Wagner and F. A. Long, *J. Phys. & Colloid Chem.*, **55**, 1512 (1951).

[7] A. Katchalsky and I. R. Miller, *J. Polymer Sci.*, **13**, 57 (1954).

[8] I. R. Miller, *J. Colloid Sci.*, **9**, 579 (1954).

polysoaps[9-13] by Fuoss, Strauss and others. One of the present authors has studied this polymer as an emulsifying agent[14] in the polymerization of acrylonitrile in an acidic medium; he has also studied some properties of the aqueous solution of a polysoap[15] derived from poly-2-vinylpyridine. As for poly-2-vinylpyridine itself, however, relatively few investigations have been reported.

It is considered that studies of the polymerization, the fractionation, the relation between the intrinsic viscosity and molecular weight, etc., are important for the practical use of this polymer. In addition, by investigating the solution properties of the polymer, it may be possible to obtain some information about the effect of the polarity of pyridine nitrogen on its solubility and conformation in a solution. Recently, the effect of the tacticity of a polymer on solution behavior has become an interesting subject; data in this field have been collected for many polymers. Isotactic crystalline poly-2-vinylpyridine was first polymerized by Natta and others[16] in 1960 using Grignard's reagent as a catalyst. As both isotactic and atactic poly-2-vinylpyridine are soluble in various solvents at ordinary temperatures, they are considered to be suitable samples for the investigation into the effect of tacticity on the solution properties.

In the present work, the suspension polymerization of 2-vinylpyridine was studied with regard to the effect of the concentrations of the stabilizer and the initiator and to that of the temperature. The results of the study of the molecular weight distribution of the polymer will also be reported here.

Experimental

Materials. — 2-Vinylpyridine monomer (Tokyo Yukigoseikogyo Inc.) was distilled immediately before use under a vacuum with a 100-cm. jacketed column containing Podvielniak single-turn helix packing. A middle portion (b. p. 71°C/32 mmHg) was used for polymerization. All the solvents were purified by the usual procedure. Sodium butylnaphthalene sulfonate (Pelex-NBK, Kao Sekken Inc.) was purified by recrystallization.

Polymerization.—2-Vinylpyridine was polymerized in a sealed glass ampoule under a nitrogen atmosphere by the suspension method. Gelatine and Pelex-NBK were used as stabilizers, and azo-bis-isobutyronitrile (AIBN), as an initiator. An aqueous solution of gelatine and Pelex-NBK and a monomer in which AIBN had been dissolved under cooling were introduced in an ampoule successively. The ampoule was then cooled with a mixture of dry ice and acetone, and the air was replaced by a nitrogen atomsphere. After the ampoule had been sealed, polymerization was performed in a water bath with stirring by the revolution of the ampoule. After the required time, the polymerization was stopped by pouring the suspension into a large amount of water. The supernatant liquid was decanted off after most of polymer particles had precipitated. The particles were washed at least four times with hot water on a No. 2 sintered glass filter.

Intrinsic Viscosity.—A modified Ubbelohde-type viscometer was used for the measurement of the viscosity. The flow time for 92.01 weight per cent ethanol varied from 120 to 300 sec. according to the viscometer used. All the solutions were filtered through a No. 3 sintered glass filter immediately before measurement and were successively diluted in the viscometer. The initial concentration was determined by a weighing method. The intrinsic viscosity $[\eta]$, was obtained according to Eq. 1:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (1)$$

where η_{sp} is the specific viscosity; c, the concentration of the polymer in g./100 ml., and k', Huggins' constant.

Osmotic Pressure.—The osmotic pressure was measured statically with a Zimm-Myerson-type osmometer (Shibayama Rikagaku Kikai Seizosho) at 25± 0.003°C. Gel cellophane No. 300 (Tokyo Serohanshi Inc.) was used as the membrane after the usual treatment. The leakage of low-molecular-weight polymer through the membrane could not be prevented because all the samples were unfractionated polymers. Thus, the pressure decreased slowly and linearly after the attainment of an apparent equilibrium. Consequently, the measurement was carried on for 5 or 6 days, employing the method of extrapolation to zero time. The number-average molecular weight, M_n, was obtained according to Eq. 2:

$$\pi/c = \boldsymbol{R}T(1/M_n + A_2 c) \qquad (2)$$

where π is the osmotic pressure; $\boldsymbol{R}$, the gas constant; T, the absolute temperature, and A_2, the second virial coefficient.

Light Scattering.—Light scattering was measured with a Brice-type microphotometer (Shimadzu Seisakusho Inc.) with unpolarized and monochromatized incident light (436 mμ) and using the dissymmetry method. The refractive index increment was measured with a Debye-type instrument (Shimadzu Seisakusho Inc.). Data were arranged according to Eq. 3:

$$Kc/R_\theta = 1/\{M_w P(\theta)\} + 2A_2 c \qquad (3)$$

where $K = 2\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2/(\lambda^4 \boldsymbol{N})$

and where n_0 is the refractive index of solvent: $\mathrm{d}n/\mathrm{d}c$, the refractive index increment; λ, the wavelength of incident light; $\boldsymbol{N}$, the Avogadro number; R_θ, the reduced intensity of scattered light at an angle of θ, and $1/P(\theta)$, the dissymmetry correction. $[Kc/R_\theta]_0$ was obtained by the extrapolation of the linear line obtained by plotting Kc/R_θ versus c, while $1/P(90)$ was obtained from the dissymmetry, $z=[Kc/R_{135}]_0/[Kc/R_{45}]_0$, using the table

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9) U. P. Strauss and E. G. Jackson, *J. Polymer Sci.*, **6**, 649 (1951).

10) L. H. Layton, E. G. Jackson and U. P. Strauss, ibid., **9**, 295 (1952).

11) L. H. Layton and U. P. Strauss, *J. Colloid Sci.*, **9**, 149 (1954).

12) U. P. Strauss and S. S. Slowata, *J. Phys. Chem.*, **61**, 411 (1957).

13) H. E. Jorgensen and U. P. Strauss, ibid., **65**, 1873 (1961).

14) S. Arichi, *J. Sci. Hiroshima Univ. Ser. A-II*, **25**, 419 (1962).

15) M. Miura, S. Arichi and T. Morita, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 32 (1962).

16) G. Natta, G. Mazzanti, G. Dall'Asta and P. Longi, *Makromol. Chem.*, **37**, 160 (1960).

TABLE I. THE EXPERIMENTAL RESULTS OF POLYMERIZATION[a)]

Sample No.	Temp. °C	Concn. of AIBN[b)]	Time hr.	Conv. %	$[\eta]$[c)] dl./g.	M_w $\times 10^{-4}$	M_n $\times 10^{-4}$	M_w/M_n
9	85	1.5	6	84.2	0.41	8.12		
10	85	1.0	6	80.8	0.49	9.10		
11	85	0.5	6	87.8	0.59			
12	85	0.1	6	74.8	0.94	21.10	5.57	3.8
1	65	2.5	12	91.8	0.56	14.27	4.15	3.4
2	65	1.5	12	82.4	0.64		4.91	
3	65	0.5	12	79.7	0.86	19.74		
4	65	0.2	12	45.0	0.90			
5	45	1.0	96	92.1	1.17	27.23	6.66	4.1
6	45	0.5	96	67.7	1.29	32.40	7.73	4.2
7	45	0.1	137	37.5	1.69			
8	45	0.05	137	34.9	1.48	39.10	8.00	4.9
13	40	0.2	288	58.7	—[d)]			
14	40	0.1	288	49.2	—[d)]			

a) Weight ratio of water to monomer was 2 : 1, the concentrations of gelatine and Pelex-NBK were 0.75 and 0.025 per cent with respect to water.

b) Weight per cent with respect to monomer.

c) In 92.01 weight per cent ethanol at 25±0.01°C.

d) The polymer did not dissolve in hot solvent within a month.

of Doty and Steiner[17)] for the unfractionated polymers. The instrument was calibrated with benzene which had been purified by three recrystallizations and distillations, using $R_{90}=48.5\times10^{-6}$ (436 mμ).[18)]

Fractionation.—The fractional precipitation method was used. Ethyl methyl ketone and ligroin were used as a pair, as a solvent and a precipitant. The polymer solution (of 1 or 2 weight per cent) was poured into a heart-type flask, and then ligroin was added slowly while the solution was stirred vigorously at 30°C. After the appearance of a proper turbidity, stirring was still continued for 1 or 2 more hours; then the system was allowed to stand overnight. The gel thus obtained was separated from the supernatant liquid by decantation. A solid polymer was obtained by pouring excessive petroleum ether into the gel. The product was washed with petroleum ether and dried in a vacuum dryer.

Results and Discussion

The Effect of Concentrations of Gelatine and Pelex-NBK on the Stability of the Suspension.—The effect of concentrations of gelatine and Pelex-NBK on the stability of the suspension was investigated with a 20 ml. ampoule scale. The polymerization conditions were as follows: water, 10 g.; monomer, 5 g.; AIBN, 0.1 g.; temperature, 45°C and revolution velocity of ampoule, 40 r. p. m. while the concentrations of gelatine and Pelex-NBK varied. After 5 hours' polymerization, the states of suspension were observed and the diameter of particles was measured with a microscope.

Neither gelatine and Pelex-NBK, when used separately, had any dispersion power up to the concentrations of 2.0 and 0.5 weight per cent respectively in water. Even when they were used as a mixture, the stability of the suspension was poor, regardless of the concentration of gelatine, until the concentration of Pelex-NBK was 0.02 per cent. When the concentrations of gelatine and Pelex-NBK exceeded 0.75 and 0.025 per cent respectively, however, the suspension became very stable; the stability showed no remarkable change with the concentrations of gelatine and Pelex-NBK until they were 1 and 0.75 per cent respectively. However, the size of the particle became smaller and the polydispersity decreased wtih the increase in the concentration of gelatine at a constant concentration of Pelex-NBK.

The diameter of most particles was smaller than ca. 0.2 mm. There was also a small amount of very fine particles.

The Effect of the Concentration of AIBN and of the Temperature on the Conversion and the Intrinsic Viscosity of the Polymer.—The polymerization for the preparation of samples was performed in a 400 ml. ampoule. The conditions were as follows; the weight ratio of water to the monomer was 2 : 1; the concentrations of gelatine and Pelex-NBK were 0.75 and 0.025 weight per cent in water respectively; the revolution velocity of ampoule was 40 r.p.m., and the concentrations of AIBN and the temperature varied. The intrinsic viscosity of the polymer solutions in 92.01 weight per cent ethanol was measured at 25±0.01°C.

The results of polymerization are shown in Table I. As may be seen in this table, the conversion is sufficiently high in most cases. When we denote the concentration of AIBN as p (weight per cent with respect to the monomer), the relation between $p^{-1/2}$ and $[\eta]$ at each temperature is

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17) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).

18) C. I. Carr and B. H. Zimm, ibid., **18**, 1616 (1950).

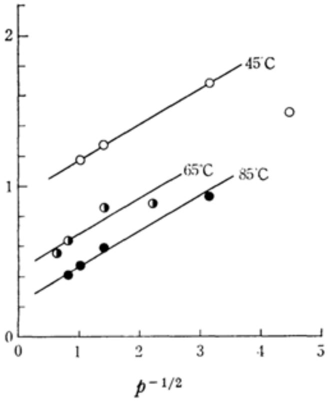

Fig. 1. Effect of AIBN concentration, p (weight per cent with respect to monomer), on the intrinsic viscosity of poly-2-vinylpyridine at constant temperature indicated.

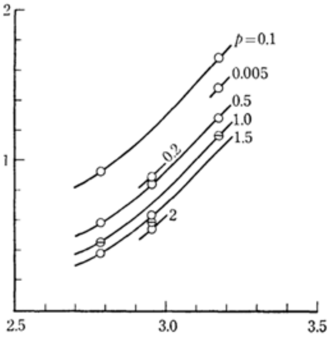

Fig. 2. Effect of temperature on the intrinsic viscosity of poly-2-vinylpyridine at constant concentration of AIBN indicated.

linear except at a very low concentration of catalyst, as may be seen in Fig. 1.

The relation between $1/T°K$ and $[\eta]$ at a constant concentration of AIBN is shown in Fig. 2. The temperature dependence of $[\eta]$ seems to be nearly the same for all the concentrations of AIBN studied. It is apparent that, in the present method of suspension polymerization, it is possible to control the molecular weight of the polymer by varying the concentration of AIBN and the temperature.

The Weight-average and Number-average Molecular Weight of the Polymer.—The M_w and M_n values of several samples were determined by measuring the light scattering of the polymer in methanol and the osmotic pressure of the polymer solution in ethyl methyl ketone respectively. The results are shown in Figs. 3 and 4 and are summarized in Table I. The values of M_w/M_n given in column 9 of the table show that the width of the molecular weight distribution of the polymers is quite large, but the values do not vary very much with polymerization conditions.

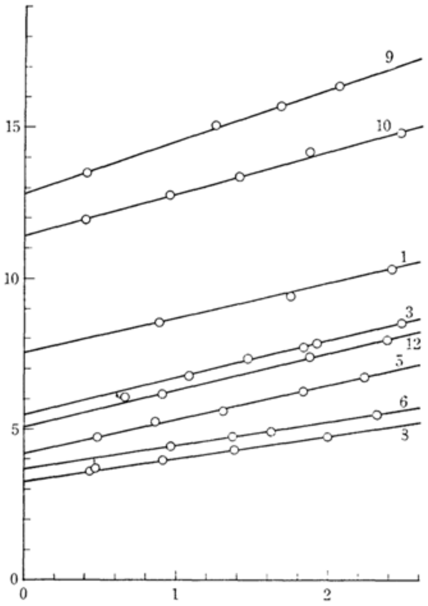

Fig. 3. Plots of reciprocal reduced scattering intensity vs. concentration of poly-2-vinylpyridine in methanol at 25°C.

In Fig. 5 the intrinsic viscosity in 92.01 weight per cent ethanol is plotted against the M_w and M_n values in double logarithmic scales. Sufficiently exact information has been obtained on the relation between the intrinsic viscosity and the molecular weight of the polymer obtained under the experimental conditions described. The results on the fractionated polymers will be reported in Part III.[19]

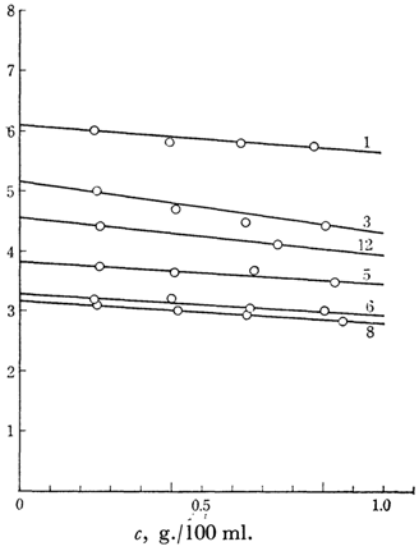

Fig. 4. Plots of reduced osmotic pressure vs. concentration of poly-2-vinylpyridine in ethyl methyl ketone at 25°C.

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[19] S. Arichi, This Bulletin, **39**, 439 (1966).

TABLE II. RESULTS OF FRACTIONATION

Primary fractionation

	Sample No.	W_i g.	$[\eta]$ dl./g.
Input	6	61.6	1.29
Output	6A	17.1	2.23
	6B	12.9	1.66
	6C	13.6	1.19
	6D	18.9	0.68
	6E	1.1	0.16

Secondary fractionation

	Sample No.	W_i g.	$[\eta]_i$ dl./g.	$W_i/\sum W_i$ %
Input	6A	16.6	2.23	—
Output	6A-1	2.48	3.01	4.51
	6A-2	1.98	2.57	3.60
	6A-3	1.62	2.51	2.94
	6A-4	1.53	2.34	2.78
	6A-5	1.42	2.23	2.58
	6A-6	1.42	2.27	2.56
	6A-7	1.68	1.61	3.05
	6A-8	1.04	1.36	1.89
	6A-9	1.73	0.89	3.14
Input	6B	12.2	1.66	—
Output	6B-1	2.38	2.09	4.32
	6B-2	2.07	2.03	3.76
	6B-3	0.80	1.83	1.45
	6B-4	1.00	1.45	1.82
	6B-5	1.00	1.45	1.82
	6B-6	0.74	1.50	1.34
	6B-7	0.71	1.36	1.29
	6B-8	0.96	1.26	1.74
	6B-9	0.57	1.09	1.04
	6B-10	0.50	0.54	0.91
Input	6C	13.1	1.19	—
Output	6C-1	1.20	1.55	2.18
	6C-2	1.40	1.69	2.54
	6C-3	0.99	1.51	1.80
	6C-4	1.61	1.48	2.93
	6C-5	1.38	0.86	2.51
	6C-6	1.37	0.90	2.49
	6C-7	1.97	0.52	3.58
	6C-8	1.70	0.66	3.09
Input	6D	17.8	0.68	—
Output	6D-1	1.91	1.09	3.47
	6D-2	1.38	0.83	2.51
	6D-3	1.54	0.71	2.80
	6D-4	1.51	0.58	2.87
	6D-5	1.41	0.51	2.56
	6D-6	1.71	0.84	3.11
	6D-7	2.46	0.58	4.47
	6D-8	2.00	0.41	3.63
	6D-9	2.71	0.23	4.92

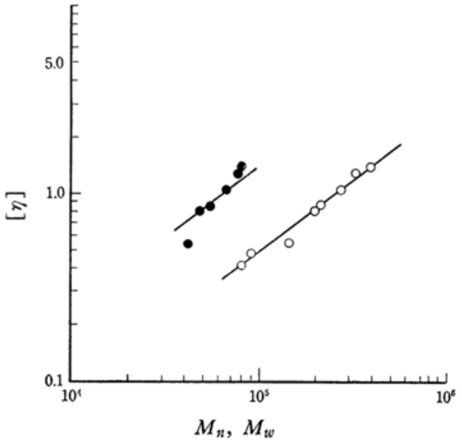

Fig. 5. Log-log plots of $[\eta]$ vs. M_n (-●-) and of $[\eta]$ vs. M_w (-○-) in 92.01 weight per cent ethanol at 25°C for unfractionated poly-2-vinylpyridine.

Results of Fractionation.—Unfractionated poly-2-vinylpyridine (No. 6 listed in Table I) was chosen as the sample for the measurement of the molecular weight distribution. Using the method described previously, 61.6 g. of this polymer was fractionated into five fractions; each of the first four fractions was refractionated into eight or ten subfractions, and the intrinsic viscosity was measured in 92.01 weight per cent ethanol at 25±0.01°C. The results of fractionation are shown in Table II.

The Molecular Weight Distribution (MWD) Curve.—Three kinds of MWD curves were obtained by applying the data in Table II to (1) Tung's method,[20] which is a modification of Schulz',[21] (2) exponential-type[22] and (3) logarithmic normal-type MWD functions[23] respectively.

Schulz-Tung's Method.—According to Tung,[20] the S-shape integral distribution, $I(M)$, was assumed to be given by:

$$I(M) = 1 - \exp(-aM^b) \qquad (4)$$

If $\log[1/\{1-I(M)\}]$ is plotted against M on a double logarithmic paper, the plots will fall on a straight line with a slope of b and an intercept of $\log(a\log e)$. The differential weight distribution function, $w(M)$, can be obtained from Eq. 4 as follows:

$$w(M) = \mathrm{d}I(M)/\mathrm{d}M = ab\exp(-aM^b)M^{b-1} \qquad (5)$$

When the molecular weight, M, is replaced by the intrinsic viscosity, the constants a and b are

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[20] L. H. Tung, *J. Polymer Sci.*, **20**, 495 (1956).

[21] G. V. Schulz and A. Dinglinger, *Z. physik. Chem.*, **B43**, 47 (1939).

[22] G. V. Schulz, ibid., **B30**, 379 (1935); B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948).

[23] R. Koningsveld and C. A. F. Tuijnman, *J. Polymer Sci.*, **39**, 445 (1959).

replaced by a' and b'; the relations among them are given[24] by:

$$a' = aK'^{-b/\nu}, \quad b' = b/\nu$$

where K' and ν are the constants in the Mark-Houwink equation, $[\eta]=K'M^{\nu}$.

The Tung plot is shown in Fig. 6. The values of a' and b' obtained from this figure are 0.532 and 1.60 respectively. As will be shown in Part III,[19] the Mark-Houwink equation with fractionated poly-2-vinylpyridine in 92.01 weight per cent ethanol at 25±0.01°C is expressed by $[\eta]=1.22\times10^{-4}M_w^{0.73}$. Using this equation and the values of a' and b' obtained above, the values of a and b are calculated to be 2.95×10^{-7} and 1.17 respectively. The calculated $w(M)$ value is shown in Fig. 7 by curve I.

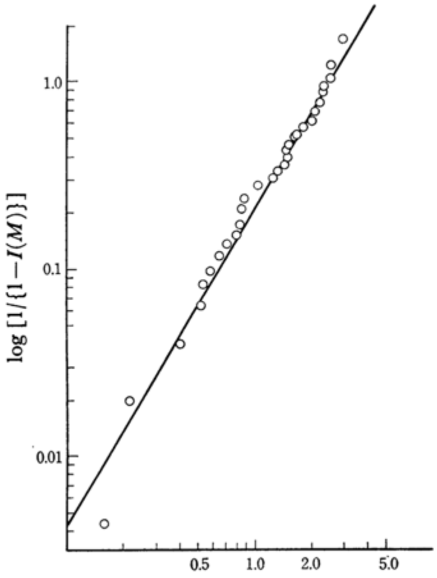

Fig. 6. Fractionation data for poly-2-vinylpyridine (sample, No. 6) arranged by Tung's method.

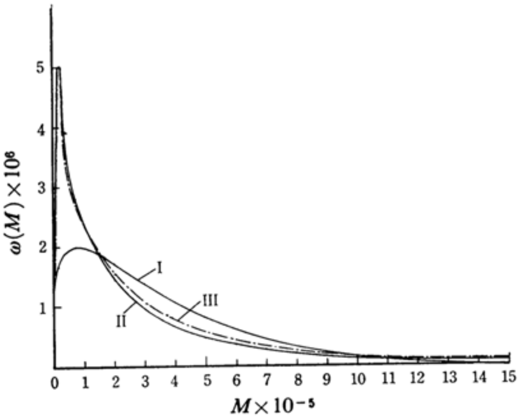

Fig. 7. Differential weight distribution curves of poly-2-vinylpyridine (sample, No. 6).
I Tung's method, II Exponential type,
III Logarithmic normal type

The Exponential-type MWD Curve.—The MWD function proposed by Schulz and Zimm[22] and treated by the statistical method of Booth and Beason[25] is expressed by Eqs. 6 and 7:

$$w_i(M)=\{Y_i^{h_i+1}/\Gamma(h_i+1)\}M^{h_i}\exp(-Y_iM) \quad (6)$$

$$w(M)=\sum w_i(M) \quad (7)$$

where $w_i(M)$ and $w(M)$ are differential MWD functions of the ith fraction and the original polymer respectively. Parameters Y_i and h_i are related by Eq. 8 to the molecular weights, M_{w_i} and M_{n_i} of the ith fraction:

$$Y_i = h_i/M_{n_i} = (h_i+1)/M_{w_i} \quad (8)$$

In this work, these parameters for each fraction were calculated from the values of M_{w_i} and M_{n_i} which had been obtained from the Mark-Houwink equation for M_w described above and that for M_n[19]; $[\eta]=2.13\times10^{-4}M_n^{0.73}$. The result for MWD is shown by the curve II in Fig. 7.

The Logarithmic Normal-type MWD Curve.—The logarithmic normal distribution function proposed by Koningsveld and Tuijinman[23] is expressed by Eq. 9:

$$w_i(M) = MA_i\exp\{-p_i^2(\ln M/M_{oi})^2\} \quad (9)$$

where $w_i(M)$ is the differential weight distribution function of the ith fraction and A_i, a parameter normalizing the function to a desired total number of weight; p_i, a parameter related to the width of the distribution; and M_{oi}, the molecular weight at which the function reaches its maximum value. The values of A_i, p_i and M_{oi} can be calculated by the following equations, using the average molecular weights, M_{w_i} and M_{n_i}, of the ith fraction:

$$A_i = (W_i/M_{w_i}M_{n_i})\exp(-1/p_i^2)(\pi^{1/2}/p_i) \quad (10)$$

$$M_{wi}/Mn_i = \exp(1/2p_i^2) \quad (11)$$

$$M_{oi} = M_{wi}/\exp(5/4p_i^2) \quad (12)$$

In this work these parameters were again obtained from the values of M_{w_i} and M_{n_i} which were calculated from the intrinsic viscosity of each fraction. The value of $w(M)$ for the original sample can be calculated by Eq. 13:

$$w(M) = \sum w_i(M) \quad (13)$$

The MWD curve thus obtained is shown by the curve III in Fig. 7.

An Examination of the MWD Curves.—As may be seen in Fig. 7, the MWD curves, II and III, closely resemble each other. Each of them has a maximum at a very low molecular weight and a characteristic long tail in the higher

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[24] J. H. Green, *Chem. & Ind.*, **1959**, 924.

[25] C. Booth and L. R. Beason, *J. Polymer Sci.*, **42**, 81 (1960).

TABLE III. COMPARISON OF $[\eta]$, M_w AND M_n OF UNFRACTIONATED POLY-2-VINYLPYRIDINE (SAMPLE No. 6)

	Obs.	Calcd.			
		From data of each fraction	From MWD curve I	From MWD curve II	From MWD curve III
$[\eta]$	1.29	$\frac{\sum W_i[\eta]_i}{\sum W_i}=1.33$	1.33	—	—
$M_w\times 10^{-4}$	32.40	$\frac{\sum W_i M_{wi}}{\sum W_i}=34.8$	36.9	29.7	31.3
$M_n\times 10^{-4}$	7.73	$\frac{\sum W_i}{\sum(W_i/W_{ni})}=6.7$	11.1	7.6	8.1
M_w/M_n	4.2	5.2	3.3	3.9	3.9

molecular weight range. In contrast to these, the curve I has a lower maximum of $w(M)$ at a higher molecular weight.

To examine the validity of these MWD curves, the M_w, M_n and $[\eta]$ values of the original polymer were calculated from these curves and compared with the experimental values. In the case of Tung's treatment, the values of M_w and $[\eta]$ were calculated by Eqs. 14 and 15[24]:

$$[\eta] = a'^{-1/b'}\Gamma(1+1/b') \qquad (14)$$

$$M_w = a^{-1/b}\Gamma(1+1/b) \qquad (15)$$

The results are shown in Table III. The values cited in column 3 of this table were calculated by means of the equations in the same column, using the weight, W_i; the intrinsic viscosity, $[\eta]_i$, and the molecular weights, M_{wi} and M_{ni}, which were obtained from $[\eta]_i$. From these values the Mark-Houwink equations described above have been proved to be applicable to the fractions in this study.

In Table III it is noticeable that the values of M_w and M_n from the exponential-type MWD curve, II, and those from the logarithmic normal-type one, III, are in good agreement with the experimental values. On the other hand, those from Tung's method, I, are considerably larger than the experimental values. These results show that the MWD of each fraction is well represented by the above two functions; they also show that the overlapping of various molecular weights in each fraction can not be neglected in reality. These results resemble closely those for isotactic polypropyrene reported by Kotera and others.[26]

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[26] A. Kotera, K. Takamizawa, T. Kamata, H. Kawaguchi, M. Nireki, M. Kuwabara and K. Yamashita, presented at the 10th Symposium on High Polymers, Tokyo, November, 1961.