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Studies of Poly-2-vinylpyridine.
III. Intrinsic Viscosity and Molecular Weight

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The viscosity, osmotic pressure and light-scattering of a series of 14 fractions of poly-2-vinylpyridine in various solvents have been measured. The following results have been obtained: The constants, K_w' and ν, in the Mark-Houwink equation have been determined for the solutions of: (a) 92.01 weight per cent ethanol, (b) methanol, (c) dimethylformamide, (d) benzene and (e) dioxane as follows:

(a) $[\eta] = 1.22\times 10^{-4} M_w^{0.73}$

(b) $[\eta] = 1.13\times 10^{-4} M_w^{0.73}$

(c) $[\eta] = 1.47\times 10^{-4} M_w^{0.67}$

(d) $[\eta] = 1.70\times 10^{-4} M_w^{0.64}$

(e) $[\eta] = 3.09\times 10^{-4} M_w^{0.58}$

The molecular weight of the polymers ranged from 3.4×10^4 to 93×10^4, while the viscosity was measured at 25±0.01°C. The constant, K', in the Mark-Houwink equation in the case of a homogeneous molecular weight has been calculated assuming the exponential- and logarithmic normal-type molecular weight distribution functions for each fraction. The Flory constant, K, defined as $[\eta]_\theta = KM^{1/2}$ has been found by the method of Fixman and Krigbaum to be: $(8.7\pm 1.0)\times 10^{-4}$ at 25°C. The K value has also been found to be $(9.1\pm 1.1)\times 10^{-4}$ by measuring the intrinsic viscosity in benzene at the θ-point, 16.2°C. The short range interactions of this polymer have also been discussed.

The Mark-Houwink viscosity equation and the unperturbed chain dimension of poly-2-vinylpyridine have not been reported in spite of their importance in the investigation of the polymer solution. The Mark-Houwink equation for poly-4-vinylpyridine, which, in chemical structure, closely resembles poly-2-vinylpyridine, has been reported by Strauss¹⁾ and Fuoss²⁾, and the data concerning to the unperturbed chain dimension of poly-4-vinylpyridine, together with those of many other polymers, have recently been summarized by Kurata and Stockmayer.³⁾ The Mark-Houwink equation for poly-2-vinylpyridine may not be so much different from that of poly-4-vinylpyridine. However, the solubility characters of these two polymers in certain solvents differ from each other, as has been shown in Part II⁴⁾; so it is considered important to obtain the equation for poly-2-vinylpyridine. In addition, by comparing the unperturbed chain dimension of poly-2-vinylpyridine with those of poly-4-vinylpyridine and polystyrene, it may be possible to obtain information about the effect of the polarity and the structural position of pyridine nitrogen on the conformation of the polymers in solution.

As most polymer samples have a distribution

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1) A. G. Boyes and U. P. Strauss, *J. Polymer Sci.*, **22**, 463 (1956).

2) J. B. Berkowitz, M. Yamin and R. M. Fuoss, ibid., **28**, 69 (1958).

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

4) S. Arichi, H. Matsuura, Y. Tanimoto and H. Murata, This Bulletin, **39**, 434 (1966).

of molecular weight, corrections for the distribution must be applied to the experimentally obtained parameters, such as the constants, K' in the Mark-Houwink equation and K in the Flory equation. These corrections can be made by means of the proper equation based on a molecular weight distribution function; in this case the M_w/M_n ratio of the sample is always an important factor. In this study, both M_w and M_n were measured for 14 fractions of poly-2-vinylpyridine, and corrected values of the constants in the Mark-Houwink equation in five solvents and the unperturbed dimensions of the polymer were obtained.

Experimental

Polymers.—The polymer samples used in this investigation were prepared by the fractionation of the original polymers, which were described in Part I.[5] The composition of the solvent-precipitant and the technique of the fractionation were similar to those reported previously.[5] Each of the ten original polymers was first divided into 3 or 5 fractions; the fractions whose intrinsic viscosities were close to one another were put together. Thus, 13 fractions were obtained, they were named A, B, C, etc. Each of these fractions was then refractionated into three fractions, which were denoted A-1, A-2, A-3, B-1, etc.; of these, the middle fractions (A-2, B-2, C-2, etc.) were mainly used in this investigation.

In order to obtain the fractions whose molecular weights are higher than those obtained by the above method, the polymerization was performed by the method of Pritchard and others,[6] using potassium persulfate-sodium bisulfite as a redox initiator in an aqueous solution of the monomer acidified with hydrochloric acid at 45°C. The polymer was then fractionated as has been described above. Two of the resultant fractions N-3 and N-4, were used in this study.

Solvents.—The solvents used were guaranteed or first class reagents and were distilled before use, as has been described in Part I.[5]

The Phase Separation Temperature.—The polymer-solvent phase separation temperature was measured using a heart-type flask, to which a reflux condenser, a drying column containing phosphorous pentoxide and a glass stirrer were attached.

Viscosity, Osmotic Pressure and Light-scattering.—All apparatus for the measurement of viscosity, osmotic pressure, light-scattering and the refractive index increment were described in Part I.[5] The viscosities of a series of fractions were mesaured in various solvents at 25±0.01°C by the method of dilution in a viscometer. The correction for kinetic energy was neglected. The osmotic pressure was measured by a static method at 25±0.003°C, using a gel cellophane membrane (No. 300). No leakage of the solute molecule through the membrane was observed except for the sample with the lowest molecular weight (A-2, $M_w=3.40\times10^4$); within 6 to 12 hr. the pressure reached an equilibrium which showed no change even after 24 hr. The reproducibility was checked by the reduced osmotic pressures, $(\pi/c)_0$, measured three times with the E-2 fraction in methanol, which were 3.41 3.43, and 3.30 ($\times10^2$ cm.).

Light-scattering was measured by a dissymmetry method with unpolarized incident light (436 mμ) at 25±1°C. The instrument was calibrated by using benzene[7] and also by means of a standard scattering plate.[8] The instrumental constants obtained by these two methods agreed with each other within the range of experimental error. The values of the molecular weight of the standard polystyrene, MS-1,[9] determined by using this instrumental constant were 23.7×10^4 and 23.6×10^4; these values were in good agreement with the mean value reported.[9] The solution and solvent were filtered through a cellafilter, "fein" or "mittel" (Membran Geselschaft, Göttingen, Germany). The concentration of the solution was determined by a weighing method. The dissymmetry was determined by the $[Kc/R_{135}]_0/[Kc/R_{45}]_0$ ratio, which was corrected for the back reflection of the incident light.

Results and Discussion

The Intrinsic Viscosity.—The results of the viscosity measurement of a series of fractions in methanol at 25±0.01°C are shown in Fig. 1. The measurements were also carried out for the same fractions in 92.01 weight per cent ethanol, dimethylformamide, benzene and dioxane.

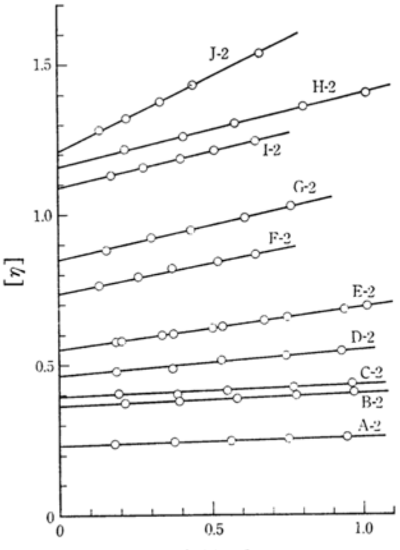

Fig. 1. Plots of reduced viscosity vs. concentration of poly-2-vinylpyridine fractions in methanol at 25°C.

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[5] S. Arichi, S. Mitsuta, N. Sakamoto and H. Murata, ibid., **39**, 428 (1966).

[6] J. E. Pritchard, M. H. Opheim and P. H. Moyer, *Ind. Eng. Chem.*, **47**, 863 (1955).

[7] C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 1616 (1950).

[8] B. A. Brice, M. Halwer and R. Speiser, *J. Opt. Soc. Am.*, **40**, 768 (1950).

[9] The Committee on Molecular Weight and Molecular Weight Distribution, *Rept. Progr. Polymer Phys. Japan*, **4**, 141 (1960).

The Osmotic Pressure.—The results of the measurement of the osmotic pressure of a series of fractions in methanol at 25±0.003°C are shown in Fig. 3. The results for the H-2 fraction in ethanol, methanol, isopropanol, benzene and ethyl methyl ketone were presented earlier, in Part II.4)

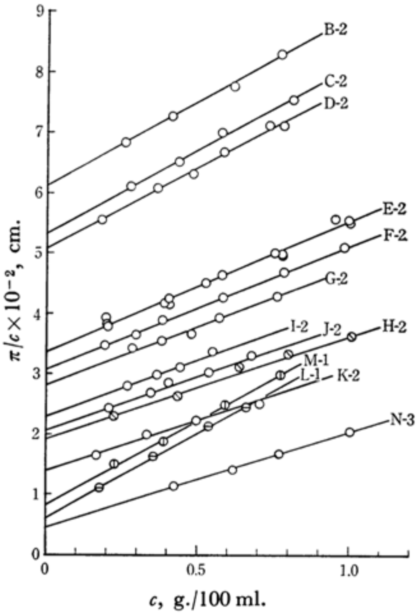

Fig. 2. Plots of reduced osmotic pressure vs. concentration of poly-2-vinylpyridine fractions in methanol at 25°C.

The Light-scattering.—The light-scattering of several of the fractions was measured in methanol, ethanol, isopropanol, ethyl methyl ketone, dioxane and benzene. In spite of the normal behavior shown in R_{90}, the angular distribution of scattered light showed a noticeable abnormality in all solvents; an extremely small dissymmetry (sometimes less than unity) was observed over the whole range of concentrations measured. A typical example is shown in Fig. 3 by the Zimm plot. The same behavior was observed irrespective of whether the incident light was polarized or unpolarized.

An abnormalilty in the angular distribution has also been reported by Miura and others10) for poly-2-methyl-5-vinylpyridine in methanol. Fuoss and others2) measured the light scattering of poly-4-vinylpyridine in absolute ethanol containing 0.02 mol. of dry ammonia per 1000 cc. "in order to suppress any possible ionization of pyridine nitrogen." In fact, an abnormal behavior in dissymmetry, which resembles that of a polyelectrolyte in a solution of a low ionic strength, has also been found for poly-2-vinylpyridine in absolute ethanol11) and in nitromethane.12)

On the other hand, no abnormality has been reported for poly-4-vinylpyridine in 92.01 weight per cent ethanol1) or for poly-2-vinylpyridine in methanol13) or in dioxane12). Since the abnormality described above was not observed in the

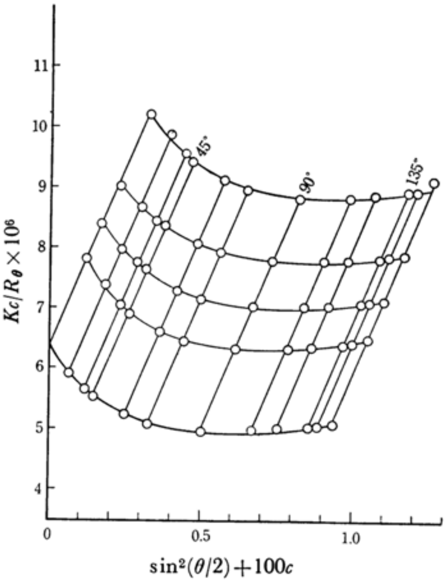

Fig. 3. The Zimm plots of faction G-2 in methanol at 25°C.

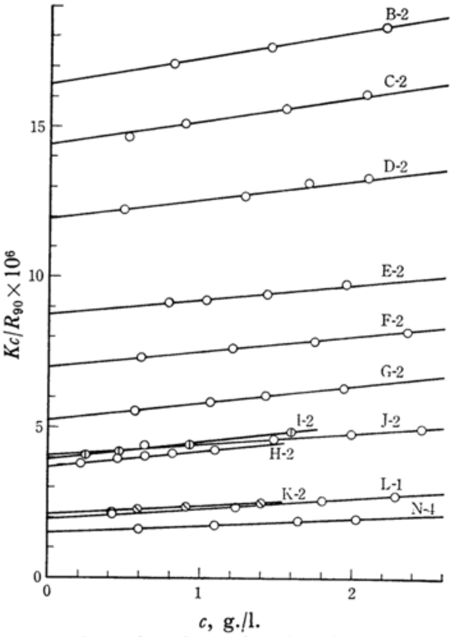

Fig. 4. Plots of reciprocal reduced intensity vs. concetration of poly-2-vinylpyridine fractions in methanol contained 0.02 mol. of dry ammonia per 1000 cc. at 25°C.

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10) M. Miura, Y. Kubota and T. Masuzukawa, This Bulletin, **38**, 316 (1965).

11) A. J. Hyde and R. B. Taylor, *Makromol. Chem.*, **62**, 204 (1963).

12) W. M. Cashin, *J. Colloid Sci.*, **6**, 271 (1951).

13) H. Inoue, *Kolloid-Z. u. Z. Polymere*, **195**, 102 (1964).

TABLE I. THE RESULTS OF LIGHT SCATTERING, OSMOTIC PRESSURE AND VISCOSITY MEASUREMENT FOR A SERIES OF FRACTIONS OF POLY-2-VINYLPYRIDINE

P2VP No.	M_w $\times 10^{-4}$	M_n $\times 10^{-4}$	M_w/M_n	$(A_2)_{LS}$ $\times 10^4$	$(A_2)_{OP}$ $\times 10^4$	z	$\langle L^2\rangle^{1/2}$ Å	[η] (dl./g.) in				
								92.01 wt. % Ethanol	Methanol	DMF	Benzene	Dioxane
A-2	3.04	—	—	8.10	—	1.04	250	0.255	0.230	0.160	0.140	0.134
B-2	6.28	4.15	1.51	8.24	11.4	1.06	315	0.399	0.361	0.250	0.201	0.200
C-2	7.27	4.77	1.52	7.75	11.1	1.07	342	0.420	0.394	0.280	0.220	0.214
D-2	9.30	5.00	1.86	5.67	10.7	1.07	342	0.498	0.462	0.308	0.259	0.231
E-2	12.01	7.42	1.62	5.30	8.3	1.08	368	0.636	0.550	0.360	0.305	0.275
F-2	16.05	8.16	1.97	6.62	8.0	1.18	559	0.838	0.735	0.471	0.374	0.340
G-2	21.95	8.84	2.48	5.75	7.5	1.20	585	0.942	0.847	0.530	0.420	0.371
H-2	30.08	12.97	2.32	6.20	6.3	1.16	532	1.30	1.16	0.700	0.530	0.460
I-2	31.10	10.95	2.84	6.00	7.3	1.25	651	1.20	1.09	0.640	0.502	0.441
J-2	30.75	12.10	2.54	4.56	6.9	1.29	693	1.30	1.21	0.640	0.537	0.433
K-2	52.06	18.07	2.88	4.75	6.2	1.29	693	1.78	1.69	1.02	0.790	0.610
L-1	84.97	39.51	2.15	3.98	(9.7)	1.77	1130	2.47	2.41	1.44	1.13	0.870
M-1	81.29	31.60	2.57	4.23	(10.8)	1.70	1078	2.40	2.39	1.39	1.09	0.863
N-4	93.10	—	—	3.50	—	1.90	1229	2.95	2.55	1.54	1.15	0.943
N-3	—	50.58	—	—	6.1	—	—	3.50	3.15	2.42	1.63	1.34

case of unfractionated poly-2-vinylpyridine[5] it may be possible to explain this phenomenon in terms of the contamination of polymers by some electrolytes in the course of fractionation, but the dissymmetrical behavior in benzene, dioxane and ethyl methyl ketone can not be explained in the same way. This phenomenon may also arise from the optical anisotropy of segments.[14,15]

Although the origin of the abnormality has not yet been clarified, it disappeared when methanol containing 0.02 mol. of dry ammonia per 1000 cc. was used as the solvent.[2] This solvent, therefore, was used in this study for the measurement of light-scattering of a series of poly-2-vinylpyridine fractions. The results are shown in Fig. 4.

The results of the measurements of the viscosity, the osmotic pressure, and the light-scattering are summarized in Table I, where M_n and $(A_2)_{OP}$ are the number average molecular weight and the second-virial coefficient in osmometry, and where M_w, z, $\langle L^2\rangle^{1/2}$ and $(A_2)_{LS}$ are the weight average moleclar weight, the intrinsic dissymmetry, the root mean square displacement length and the second-virial coefficient in turbidimetry respectively.

Relations among A_2, M_w and $\langle L^2\rangle^{1/2}$.—The plots of A_2 versus M_w and of $\langle L^2\rangle^{1/2}$ versus M_w are shown in Figs. 5 and 6 respectively. The expressions obtained from these plots are given in Table II. The relation between A_2 and M_w is almost the same as those obtained with other linear polymer-solvent systems, such as the polystyrene-toluene system.[16]

The exponent in the relation between $\langle L^2\rangle^{1/2}$

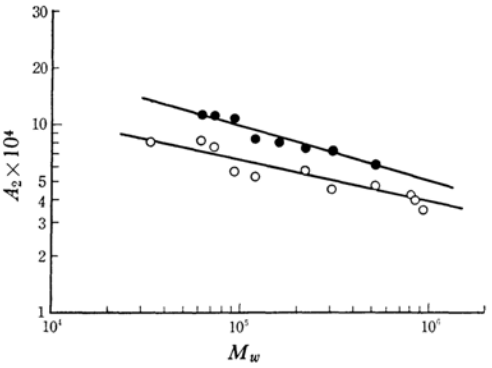

Fig. 5. Log-log plots of osmotic second virial coefficient vs. M_w in methanol (-●-) and of light scattering second virial coefficient vs. M_w in methanol contained 0.02 mol. of dry ammonia per 1000 cc. (-○-) at 25°C.

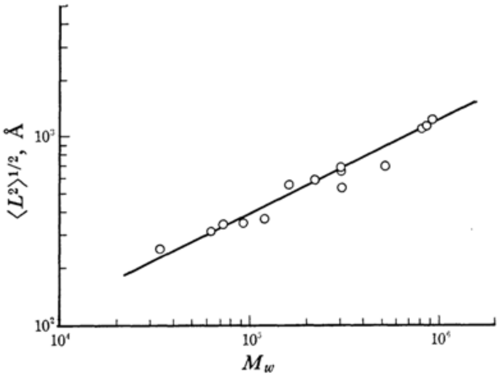

Fig. 6. Log-log plots of $\langle L^2\rangle^{1/2}$ vs. M_w for poly-2-vinylpyridine fractions in methanol contained 0.02 mol. of dry ammonia per 1000 cc. at 25°C.

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[14] M. Nakagaki, This Bulletin, **34**, 834 (1961).

[15] H. Utiyama and M. Kurata, *Bull. Inst. Chem. Research, Kyoto Univ.*, **42**, 128 (1964).

[16] E. F. Casassa and H. Markovitz, *J. Chem. Phys.*, **29**, 493 (1958).

TABLE II. RELATIONS AMONG A_2, M_w AND $\langle L^2\rangle^{1/2}$

Solvent	Temp., °C	Formula
Methanol-NH_3	25 ± 1	$(A_2)_{LS}\propto M_w^{-0.22}$
Methanol	25 ± 0.003	$(A_2)_{OP}\propto M_w^{-0.29}$
Methanol-NH_3	25 ± 1	$\langle L^2\rangle^{1/2}\propto M_w^{0.5}$

and M_w seems to be smaller than that which might be expected from the following facts: the relations between M_w and the intrinsic viscosities in pure methanol and methanol containing 0.02 mol. of dry ammonia per 1000 cc. are almost the same for all the fractions measured; moreover, methanol is an extremely good solvent for this polymer.⁴⁾

Relations among M_w, M_n and $[\eta]$.—For polymer samples which are homogeneous with respect to the molecular weight, the relation between the intrinsic viscosity and the molecular weight can be expressed by the Mark-Houwink equation:

$$[\eta] = K_i'M^{\nu} \tag{1}$$

where K_i' and ν are constants independent of the molecular weight. However, it is well known that the empirically determined values of K' in the form of Eq. 1 for heterogeneous samples vary with the kind of average, and also with the width of the distribution of the molecular weight.¹⁷⁻¹⁹⁾

In such cases, if the molecular weight distribution of the sample is known, a quantitative relation between K' and the degree of homogeneity can be obtained.²⁰,²¹⁾ For example, when the molecular weight distribution of each fraction can be represented by the exponential-type function²²⁾:

$$w(M) = \{Y^{h+1}/\Gamma(h+1)\}M^{h}\exp(-YM) \tag{2}$$

the following relations are given:

$$[\eta] = K_w'M_w^{\nu} = K_i'\{\Gamma(\nu+h+1)/\Gamma(h+1)(h+1)^{\nu}\}M_w^{\nu} \tag{3}$$

$$[\eta] = K_n'M_n^{\nu} = K_i'\{\Gamma(\nu+h+1)/\Gamma(h+1)h^{\nu}\}M_n^{\nu} \tag{4}$$

The parameters in Eq. 2 have the same meaning as in Eq. 6 in Part I,⁵⁾ while the constants, K_w' and K_n' in Eqs. 3 and 4 refer to weight and number average respectively.

On the other hand, if we take the logarithmic normal-type distribution function²³⁾:

$$w(M) = MA\exp\{-p^2(\ln M/M_0)^2\} \tag{5}$$

the relations are given by:

$$[\eta] = K_w'M_w^{\nu} = K_i'(M_w/M_n)^{\nu(\nu-1)/2}M_w^{\nu} \tag{6}$$

$$[\eta] = K_n'M_n^{\nu} = K_i'(M_w/M_n)^{\nu(\nu+1)/2}M_n^{\nu} \tag{7}$$

The parameters in Eq. 5 are the same as in Eq. 9 in Part I.⁵⁾

As the variation in the K_w' value in Eq. 3 or 6 with the change in M_w/M_n is comparatively small, the value of ν can be assumed to be nearly the same as the slope of the linear line in the double logarithmic plots of $[\eta]$ versus M_w for fractionated samples. Thus, the value of K_i' can be calculated by means of the above equations.

The intrinsic viscosities of fourteen fractions in five kinds of solvents and those in methanol are plotted against M_w and M_n respectively in Fig. 7. The plots of $[\eta]$ versus M_n can be expressed by linear lines, whereas the plots of $[\eta]$ versus M_n scatter considerably. This is considered to be due to the heterogeneity of the samples, as is shown by the M_w/M_n values cited in Table I.

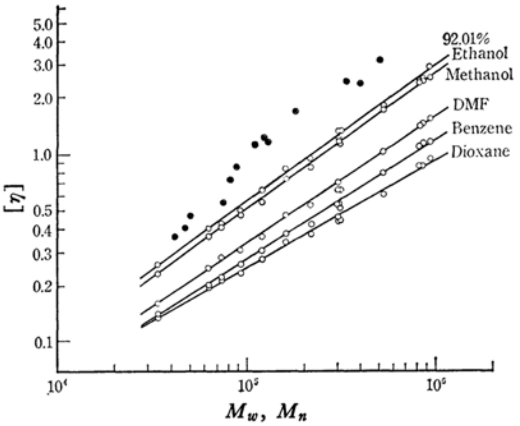

Fig. 7. Log-log plots of $[\eta]$ vs. M_n in methanol (-⊙-) and of $[\eta]$ vs. M_w in various solvents indicated (-○-) for poly-2-vinylpyridine fractions at 25°C.

The constants, ν and K_w', evaluated from the linear lines in Fig. 7 are shown in columns 2 and 3 respectively in Table III. The values of K_n' in column 4 of the table are the mean values of K_n' for all fractions; these values were calculated

TABLE III. THE CONSTANTS IN THE MARK-HOUWINK EQUATION AT 25°±0.01°C

Solvent	ν	K_w' $\times10^4$	K_n' $\times10^4$	$K_i'\times10^4$ Eqs. 3 and 4	$K_i'\times10^4$ Eqs. 6 and 7
92.01 wt.% Ethanol	0.73	1.22	2.13	1.28	1.31
Methanol	0.73	1.13	1.99	1.19	1.21
Dimethyl formamide	0.67	1.47	2.45	1.58	1.60
Benzene	0.64	1.70	2.71	1.80	1.85
Dioxane	0.58	3.09	4.78	3.30	3.38

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17) H. P. Frank and J. W. Breitenbach, *J. Polymer Sci.*, **6**, 609 (1951).

18) H. P. Frank, ibid., **7**, 567 (1951).

19) H. P. Frank and G. B. Levy, ibid., **10**, 371 (1953).

20) R. Koningsveld and C. A. F. Tuijnman, *Makromol. Chem.*, **38**, 39 (1960).

21) 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.

22) G. V. Schulz, *Z. physik. Chem.*, **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).

from the equation, $[\eta]=K_n'M_n{}^{\nu}$, the values of ν being assumed to be the same as those for the relation between $[\eta]$ and M_w.

Assuming that the molecular weight distribution of each fraction can be represented by Eqs. 2 and 5, the values of K_i' were evaluated by inserting the values of ν, K_w' and K_n' cited in Table III into Eqs. 3 and 4 and Eqs. 6 and 7. The results are shown in columns 5 and 6 of Table III.

The values of K_i' calculated by assuming the two functions given above are in good agreement with each other. The validity of the values of K_i' and ν is shown with the methanol solution, as an example, in Fig. 8. The figure in the parenthesis at each point in Fig. 8 shows the observed value of M_w/M_n. The straight lines correspond to the values of K_w' and K_n' which are obtained from Eqs. 3 and 4 by inserting the values of K_i' (1.19×10^{-4}) and ν (0.73) and the voluntarily selected values of M_w/M_n which are shown in the brackets. Almost the same results were obtained from Eqs. 6 and 7.

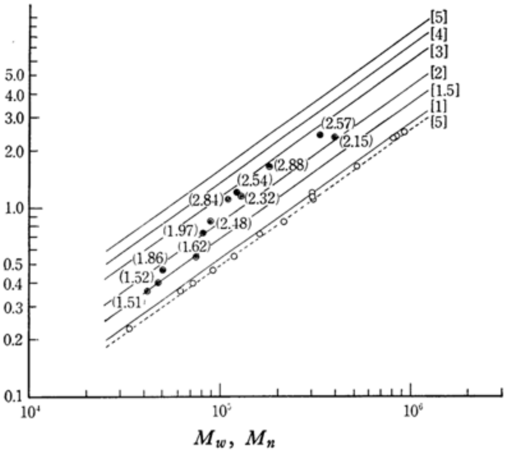

Fig. 8. Log-log plots of $[\eta]$ vs. M_w (---, Eq. 3) and $[\eta]$ vs. M_n (——, Eq. 4) for different M_w/M_n ratios indicated in [ ] assuming $K_i'=1.19\times10^{-4}$ and $\nu=0.73$ in methanol at 25°C. Points show plots of $[\eta]$ vs. M_w (-○-) and $[\eta]$ vs. M_n (-⊙-) for observed values of M_w/M_n indicated in ( ).

These results show that the values of K_i' and ν thus obtained are quite reasonable. The relation between the molecular weight and the $[\eta]$ value for sufficiently fractionated samples can be expressed by the Mark-Houwink equation containing the constants, K_i' and ν, cited in Table III.

The direction of the variation in the values of ν with the solvent is the same as the solvent power described in Part II.⁴⁾ The constants, K_w' and ν, for poly-2-vinylpyridine in 92.01 weight per cent ethanol at 25°C cited in Table III are almost the same as those for poly-4-vinylpyridine in the same solvent and temperature¹⁾:

$$[\eta]=1.20\times10^{-4}M_w{}^{0.73}$$

The Unperturbed Chain Dimension of Poly-2-vinylpyridine.—The intrinsic viscosities of a flexible linear polymer in theta and nontheta solvents are expressed by Eqs. 8 and 9 respectively²⁴⁾:

$$[\eta]_\theta=KM^{1/2} \tag{8}$$

$$[\eta]=KM^{1/2}\alpha^3 \tag{9}$$

Here K is a constant for a given polymer independent of the solvent and the molecular weight; it is related to the mean square displacement length of the chain, $\langle L^2\rangle_0{}^{1/2}$, in an ideal solvent as follows:

$$K=\Phi_0A^3, \qquad A^2=\langle L^2\rangle_0/M \tag{10}$$

where Φ_0 (0.87×10^{21}) is the universal viscosity constant for chain polymers in a theta solvent, while α in Eq. 9 is the viscosity expansion factor. According to a recent perturbation theory,²⁴⁻²⁷⁾ α is a function of $\boldsymbol{z}$, which is defined by:

$$\boldsymbol{z}=(3/2\pi)^{3/2}BA^{-3}M^{1/2} \tag{11}$$

where A is a parameter concerned with the short range interaction of segments defined by Eq. 10, and B, a parameter on the long range interaction of segments which is related to the excluded volume effect. The relation between α and $\boldsymbol{z}$ obtained by Stockmayer and Fixman²⁴⁾ is:

$$\alpha^3=1+1.55\boldsymbol{z} \tag{12}$$

From these equations they derived the following expression:

$$[\eta]/M^{1/2}=K+0.51\Phi_0BM^{1/2} \tag{13}$$

The values of $[\eta]$ and M_w cited in Table I are plotted according to this equation in Fig. 9.

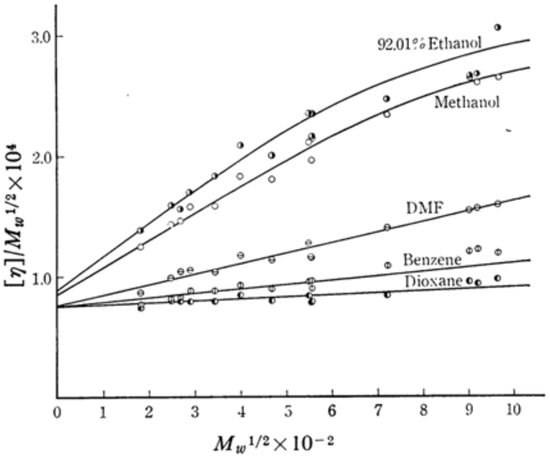

Fig. 9. Plots of $[\eta]/M_w{}^{1/2}$ vs. $M_w{}^{1/2}$ for poly-2-vinylpyridine fractions at 25°C.

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24) W. H. Stockmayer and M. Fixman, ibid., **C1**, 137 (1963).

25) M. Kurata, W. H. Stockmayer and A. Roig, *J. Chem. Phys.*, **33**, 151 (1960).

26) M. Fixman, ibid., **36**, 3123 (1962).

27) O. B. Ptitsyn and Y. Y. Eisner, *Vysokomolekulyarye Soedineniya*, **1**, 1200 (1959).

The lines for the viscosities in the relatively poor solvents, dimethylformamide, benzene and dioxane, pass through the same intercept and are linear, as was to be expected from Eq. 13, whereas the lines for the good solvents, 92.01 weight per cent ethanol and methanol, have an upward curvature and the intercepts are larger than other one. Consequently, the K_w values obtained from these intercepts lie between 7.5×10^{-4} and 8.9×10^{-4}. A similar solvent dependence of the intercept has been reported for polymethyl methacrylate.3,28,29) In Part II,4) the existence of the solvation of alcohol molecules to pyridine nitrogen was suggested; therefore, it is of interest to investigate the solvent effect30) on the unperturbed dimension of the chain. However, the present data seem insufficient for discussing this problem.

The value of K can also be obtained by the following semi-empirical equation of Krigbaum31):

$$[\eta] = [\eta]_\theta + 5.0\times10^{-3}A_2M \tag{14}$$

As has been described in Part II,4) the relation between $[\eta]$ and A_2 for the H-2 fraction in various solvents at 25°C can be expressed by Eq. 15:

$$[\eta] = 0.415 + 1.10\times10^{3}A_2 \tag{15}$$

When the value of M_w, 30.08×10^4, for the H-2 fraction is inserted into Eq. 14, the following equation can be obtained:

$$[\eta] = [\eta]_\theta + 1.50\times10^{3}A_2 \tag{16}$$

The difference between the coefficient of A_2 in Eq. 15 and that in Eq. 16 may be due to the molecular weight inhomogeneity and to experimental errors in M_w and A_2. The agreement, however, is satisfactory, and so it is reasonable to take the value of 0.415 for $[\eta]_\theta$. By inserting the values of $[\eta]_\theta$ and M_w for the H-2 fraction in Eq. 8, the value of K_w is found to be 7.6×10^{-4}. The probable error of K_w is $\pm(0.5\times10^{-4})$.

The value of K can be obtained by the more direct method, namely, by measuring the $[\eta]$ value of a fraction of poly-2-vinylpyridine in a θ-solvent. Flory and Shultz32) have derived the following relation between the critical temperature, T_c(°K), in a binary polymer-solvent system and the number of segments, x or M_w:

$$\begin{aligned}1/T_c &= (1/\theta)\{1 + (1/\psi_1)(1/x^{1/2} + 1/2x)\}\\ &\cong (1/\theta)(1 + b/M_w{}^{1/2})\end{aligned} \tag{17}$$

where θ is the theta-temperature and ψ_1, an entropy parameter.

Benzene was used as the solvent in this experiment, and the critical temperature was determined by the method of Flory32) for the E-2, J-2, K-2 and N-3 fractions. The results are plotted in Fig. 10 according to Eq. 17. The value of θ obtained from the intercept of the linear line in Fig. 10 is 16.2°C. The intrinsic viscosity of the H-2 fraction in benzene at 16.2°C was found to be 0.465; this, by definition, is the $[\eta]_\theta$ of this fraction. Thus, the value of K_w is calculated by means of Eq. 8 as 8.5×10^{-4} at 16.2°C. The probable error of K_w is $\pm(1.0\times10^{-4})$ in this case.

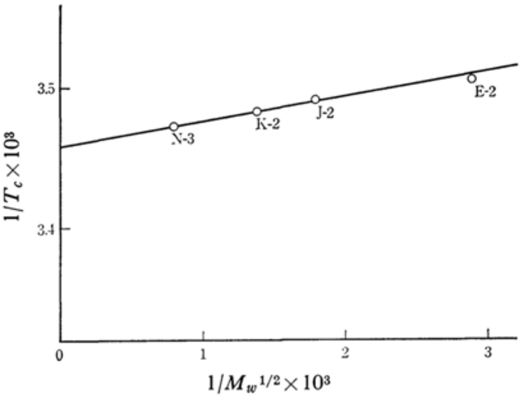

Fig. 10. Plots of reciprocal critical temperature in benzene vs. $1/M_w{}^{1/2}$ for poly-2-vinylpyridine fractions.

As the values of K_w obtained above were based on the data for samples which are not numerous enough to discuss them as a molecular homogeneous polymer, the correction for the molecular weight distribution was applied to them. Assuming again the exponential function22) for the distribution of the molecular weight, the K_w values were corrected by the following equations3):

$$[\eta]_\theta/M_w{}^{1/2} = K_w = q_wK \tag{18}$$

$$q_w = \Gamma(h+1.5)/(h+1)^{1/2}\Gamma(h+1) \tag{19}$$

As may be seen in Table I, the M_w/M_n ratio for a series of fractions is ca. 2 as a mean value, while the ratio for the H-2 fraction is 2.32. Thus, q_w was calculated by using $h=1$ for the value of K_w obtained by the Fixman plot and $h=0.758$ for the values of K_w obtained by the latter two methods. The corrected K values are shown in Table IV.

TABLE IV. CORRECTED VALUES OF THE FLORY CONSTANT, K

Method	Temp. °C	$K_w\times10^4$	q_w	$K\times10^4$
Fixman (Eq. 13)	25.0	8.2 ± 0.7	0.94	8.7 ± 0.8
Krigbaum (Eq. 14)	25.0	7.6 ± 0.5	0.93	8.2 ± 0.6
Flory (Eq. 17)	16.2	8.5 ± 1.0	0.93	9.1 ± 1.1

The K values obtained by the methods of Fixman and Krigbaum are, as may be seen in Table IV, in good agreement with each other. This implies

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28) W. Burchard, *Makromol. Chem.*, **50**, 20 (1961).

29) W. R. Moore and R. J. Fort, *J. Polymer Sci.*, **A1**, 929 (1963).

30) S. Lifson and I. Oppenheim, *J. Chem. Phys.*, **33**, 109 (1960).

31) W. R. Krigbaum, *J. Polymer Sci.*, **28**, 213 (1958).

32) A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 4760 (1952).

TABLE V. UNPERTURBED CHAIN DIMENSION CALCULATED FROM K VALUES

Polymer	Temp. °C	$K\times 10^4$	$\left[\frac{\langle L^2\rangle_0}{M}\right]^{1/2}\times 10^{11}$	$\left[\frac{\langle L^2\rangle_{0f}}{M}\right]^{1/2}\times 10^{11}$	σ	V_x
Polyethylene[3]	ca. 100	23.0 ± 3.0	950 ± 40	582	1.63 ± 0.08	8
Polystyrene[3]	ca. 30	8.2 ± 0.5	670 ± 15	302	2.22 ± 0.05	89
Poly-4-vinylpyridine[3]	25	9.4 ± 1.0	710 ± 30	300	2.37 ± 0.10	81
Poly-2-vinylpyridine	25	8.7 ± 1.0	673 ± 30	300	2.24 ± 0.10	81

that these two methods are closely correlated with each other. In fact, an extremely close resemblance between Fixman's equation (Eq. 13) and a deformation of Krigbaum's equation:

$$[\eta]/M^{1/2} = K + 0.63\Phi_0 Bh(z)M^{1/2} \qquad (20)$$

has been discussed by Stockmayer and Fixman.[24]

Considering that the hindrance to internal rotation about the C–C bond generally decreases with a rise in the temperature,[33] the value of K at 16.2°C is reasonable.

Using the values of $K = (8.7\pm 1.0)\times 10^{-4}$ and $\Phi_0 = 2.87\times 10^{21}$, the value of $[\langle L^2\rangle_0/M]^{1/2}$ for poly-2-vinylpyridine was calculated by means of Eq. 10 as $(673\pm 30)\times 10^{-11}$ at 25°C.

By denoting the unperturbed root mean square displacement length of the polymer chain in the case of free rotation about C–C bond as $\langle L^2\rangle_{0f}{}^{1/2}$, and by assuming the C–C bond length and tetrahedral angle to be 1.54 Å and 109.5° respectively, the value of $[\langle L^2\rangle_{0f}/M^{1/2}]$ was found to be 300×10^{-11}.

As a measure of the hindrance to internal rotation, the following factor, σ, was calculated for the polymer using the values of $\langle L^2\rangle_0/M$ and $\langle L^2\rangle_{0f}/M$ described above:

$$\sigma^2 = \langle L^2\rangle_0/\langle L^2\rangle_{0f} \qquad (21)$$

The results are shown in Table V, together with those[3] for polyethylene, polystyrene and poly-4-vinylpyridine. The molar volumes, V_x, of side groups of these polymers, hydrogen, the benzene ring and the pyridine ring, are shown in column 7 of Table V.

When we compare the values of σ for these four polymers, we can find relatively large σ values for the latter three polymers; these are considered to be due to the steric hindrance caused by large groups of atoms in the side chain.[3,33] Further, as the V_x value of pyridine is smaller than that of benzene, the steric hindrance to internal rotation is considered to be somewhat smaller in polyvinylpyridines than in polystyrene. In spite of this difference in the values of V_x, the values of σ for the polyvinylpyridines are, on the other hand, a little larger than that for polystyrene, as may be seen in Table V. This may be interpreted as being due to electrostatic interaction between pyridine rings.

The small difference between the σ values for poly-2-vinylpyridine and poly-4-vinylpyridine may be due to the difference in the degree of short range interactions, for example, the interaction between the nitrogen and the hydrogen in the neighboring pyridine rings or in the main chain.

However, further systematic investigation will be required to clarify this problem, together with the solvent effect on the value of K described previously.

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33) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York (1953).