Properties of the Dilute Solution of Poly-2-methyl-5-vinylpyridine

By Masaji MIURA, Yukio KUBOTA and Teruaki MASUZUKAWA

(Received July 21, 1964)

Polyvinylpyridine has been used as a source material for polyelectrolytes and polysoaps, and several studies[1,2] have given some information on its molecular dimensions. Poly-2-methyl-5-vinylpyridine (PMVP), a derivative of polyvinylpyridine, has been studied by Sato and his co-worker[3] by means of osmotic pressure measurements, but its molecular dimensions are not yet known. It is of interest, therefore, to study the properties of the dilute solution of PMVP by viscosity and light-scattering measurements.

The purpose of this investigation is (1) to establish the relationship between the intrinsic viscosity and the molecular weight of PMVP; (2) to estimate the extension of the polymer chain with the aid of recent theories on the solution behavior of high polymers,[4,5] and (3) to compare the results with those for other vinylpyridine polymers and polystyrene.

Experimental

The Preparation of PMVP.—2-Methyl-5-vinylpyridine was distilled immediately before use, and a middle fraction (b. p. 69.8—71.2°C/13 mmHg) was collected. The polymerization was carried out at 70°C for five days in a nitrogen atmosphere; the conversion rate was found to be about 40%. The polymer produced was first dissolved in methanol and then precipitated by pouring the methanol solution into a large amount of water. This was repeated twice more in order to remove the monomer which remained in the product, and then the precipitate was isolated by filtration; finally this purified material was fractionally precipitated, with methanol as a solvent and water as a precipitant. At first six fractions were obtained from a 3% methanol solution and then each fraction was separated into three to five subfractions by the same procedure, for a total of twenty subfractions; nine of these were finally selected for the viscosity and light-scattering measurements. The results of nitrogen analyses of fractions F-1-2, F-2-2 and F-6-1 were found to be 11.80, 11.94 and 11.97% respectively. These values were in good agreement with the calculated value, 11.76%.

Solvents.—The solvents used in this work were purified by the usual methods.

Viscosity.—The viscosity was measured at 25± 0.01°C with two Ubbelohde dilution viscometers, whose flow times for methanol were 114.4 sec. and 123.2 sec. The intrinsic viscosities were obtained by extrapolating the plots of the reduced viscosity, η_{sp}/C, vs. the concentration to infinite dilution.

Light Scattering. — The intensity of scattered light was measured at 25°C with both unpolarized blue (4358Å) and green light (5460Å), using a Brice-type light-scattering photometer manufactured by Shimadzu Seisakusho. All solvents and solutions were filtered into a clean semi-octagonal cell through a "Cellafilter fein or mittel" (Membranfiltergesellshaft, Göttingen) under applied pressure. Scattered intensities were measured at angles 45, 90 and 135° to the incident beam, and the data obtained were analyzed according to the usual procedure.[6] The depolarization was found to be negligible. All dissymmetries were corrected for the back reflection of the incident light.[7]

The instrument was calibrated according to two procedures; one refers to the values in the literature for the Rayleigh ratio, R_{90}, of benzene,[8] while the other utilizes standard opal glass.[9] With these calibrations, the molecular weight of the standard polystyrene sample was found to be in satisfactory agreement with the value in the literature.[10]

The refractive index increments, dn/dc, were measured at 25°C using a Debye-type differential refractometer manufactured by Shimadzu Seisakusho. The dn/dc values of PMVP in methanol were 0.273 and 0.257 at 436 and 546 mμ respectively, both at 25°C.

Results and Discussion

Abnormal light-scattering behavior, probably due to the ionization of the pyridine nitrogen, was found for all PMVP fractions in methanol. A typical example is shown in Fig. 1. Accordingly, dry ammonia gas was introduced to methanol in order to suppress any possible

---

[1] A. 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] H. Sato and T. Yamamoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1393 (1959).

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

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

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

[7] A. Oth, J. Oth and V. Desreux, *J. Polymer Sci.*, **10**, 551 (1953).

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

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

[10] Research Group of Light Scattering Standard Sample, *Chem. High Polymers* (*Kobunshi Kagaku*), **17**, 216 (1960).

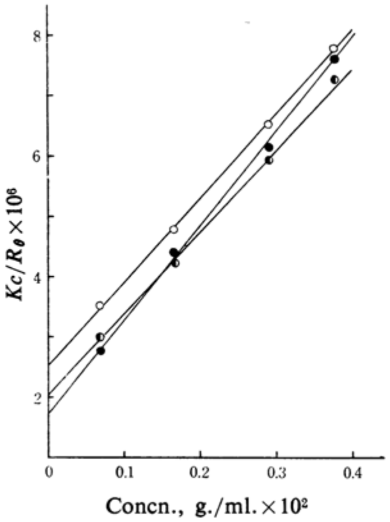

Fig. 1. Light scattering behavior of fraction F-3-2 in methanol at 4358 Å.
-○-: 135° -◐-: 90° -●-: 45°

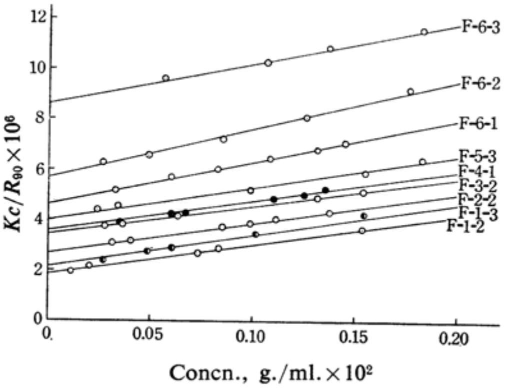

Fig. 2. Reciprocal reduced intensity, Kc/R_{90}, of PMVP fractions in methanol at 4358 Å.

ionization (0.02 M NH_3).[2] By this procedure the normal plots were obtained. The term *methanol* used hereafter denotes that methanol which contains ammonia in the amount described above. Figure 2 shows the reciprocal reduced intensity, Kc/R_{90}, of PMVP fractions in methanol at 4358 Å. The results of the viscosity and light-scattering measurements are summarized in Table I. Since the light-scattering properties are in good agreement at both wavelengths, the average values are used in the following discussion. The results of the behavior of PMVP in various solvents are summarized in Table II. There is a satisfactory agreement of the weight average molecular weight, M_w, in various solvents.

The Relation between the Intrinsic Viscosity and the Molecular Weight.—The log-log plots of the intrinsic viscosity and the molecular weight are shown in Fig. 3. In the range of the molecular weights of our samples, the plots are seen to be on a straight line. The relation between the intrinsic viscosity and the molecular weight is usually represented by the equation:

$$[\eta] = KM^a \qquad (1)$$

The constants K and a were calculated by the method of least squares, and the following equations were obtained:

TABLE I. THE RESULTS OF THE VISCOSITY AND LIGHT-SCATTERING MEASUREMENTS OF PMVP

Fraction	$[\eta]_{\text{methanol}}$ (100cc./g.)	$M_w \times 10^{-5}$			$(\overline{R^2})^{1/2}$ in Å			$A_2 \times 10^4$			$[\eta]_{\text{MEK}}$ (100cc./g.)	$[\eta]_{\text{toluene}}$ (100cc./g.)
		4358 Å	5460 Å	Av.	4358 Å	5460 Å	Av.	4358 Å	5460 Å	Av.		
F-1-2	2.53	8.61	8.99	8.80	1074	1105	1090	5.50	5.65	5.58	1.07	0.580
F-1-3	2.05	6.71	6.92	6.82	955	958	957	6.00	6.00	6.00		
F-2-2	1.70	4.83	5.08	4.96	837	845	841	5.80	6.00	5.90	0.778	0.435
F-3-2	1.46	3.88	3.97	3.93	726	739	732	5.75	6.00	5.88		
F-4-1	1.35	3.62	3.69	3.66	719	695	707	6.00	6.05	6.03	0.572	0.370
F-5-3	1.22	3.19	3.20	3.20	670	652	661	6.20	6.15	6.18		
F-6-1	1.00	2.57	2.58	2.58	559	564	562	7.65	7.55	7.60	0.490	0.307
F-6-2	0.80	1.98	2.00	1.99	496	506	501	8.00	7.90	7.95		0.275
F-6-3	0.585	1.27	1.27	1.27	408	420	414	7.50	7.60	7.55	0.302	0.218

TABLE II. THE RESULTS OF THE VISCOSITY AND LIGHT-SCATTERING MEASUREMENTS OF FRACTION F-3-2 IN VARIOUS SOLVENTS

Solvent	dn/dc	$M_w \times 10^{-5}$	$(\overline{R^2})^{1/2}$ in Å	$A_2 \times 10^4$	$[\eta]$	k'*
Methanol	0.273	4.96	841	5.90	1.70	0.353
Dioxane	0.180	4.46	644	2.35	0.97	0.353
MEK	0.219	4.33	552	1.65	0.778	0.617
Toluene	0.0951	4.94	471	−0.10	0.435	1.93

* k': Huggins' constant

$$[\eta]=0.80\times10^{-4}M_w^{0.76}$$
$$\text{in methanol at } 25^\circ\text{C} \qquad (2)$$
$$[\eta]=1.39\times10^{-4}M_w^{0.65}$$
$$\text{in MEK at } 25^\circ\text{C} \qquad (3)$$

The Dependence of the Root-Mean-Square End-to-End Distance, $(\overline{R}^2)^{1/2}$, and the Second Virial Coefficient, A_2, on the Molecular Weight.—Figure 4 shows the relation between $(\overline{R}^2)^{1/2}$ and M_w. The following equation was obtained by the method of least squares:

$$(\overline{R}^2)^{1/2}=0.49\ M_w^{0.57}$$
$$\text{in methanol at } 25^\circ\text{C} \qquad (4)$$

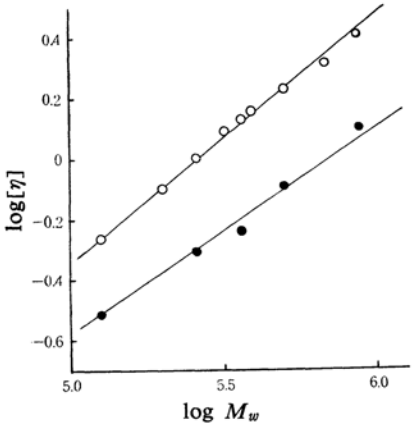

Fig. 3. Relation between intrinsic viscosity and molecular weight.
-○-: PMVPM-ethanol -●-: PMVP-MEK

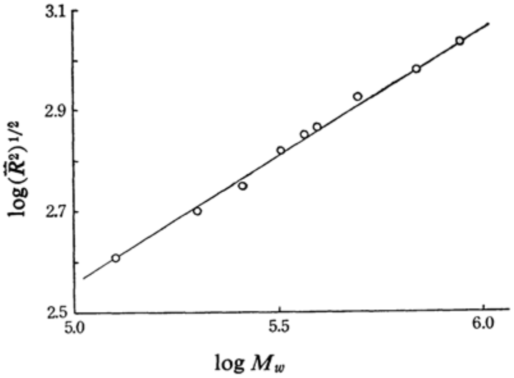

Fig. 4. Relation between root-mean-square end-to-end distance and molecular weight.

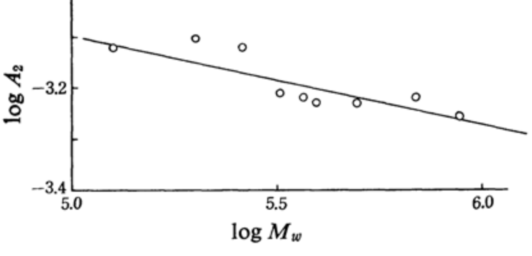

Fig. 5. Dependence of second virial coefficient on molecular weight.

As may be seen in Table I, A_2 decreases with an increase in the molecular weight. The log-log plot of A_2 and M_w in Fig. 5 gives the following relation, which is consistent with the results found for many other polymers:

$$A_2\propto M_w^{-0.20} \qquad (5)$$

Unperturbed Dimensions.—As is well known, the unperturbed dimensions may be evaluated from the data of viscosity and light scattering at the theta point.[11] The relations are:

$$[\eta]_\theta=K_0M^{1/2} \qquad (6)$$

$$K_0=\Phi_0(\overline{R}_0^2/M)^{3/2} \qquad (7)$$

where $[\eta]_\theta$ is the intrinsic viscosity in the theta solvent, $\Phi_0=2.87\times10^{21}$, and $\overline{R}_0^2$ is the unperturbed mean square end-to-end distance. As our work was not done at the theta point, the values of $[\eta]_\theta$ were not obtained directly from the experiment; $[\eta]_\theta$, however, may be determined on the basis of the $[\eta]$ and A_2 values obtained in several solvents.[12] In Fig. 6 $[\eta]$ is plotted against A_2 for fraction F-3-2 using the data in Table II. The value of $[\eta]_\theta$ was 0.46. Substituting the values for $[\eta]_\theta$ and $M(4.69\times10^5)$ into Eq. 6, we found K_0 to be 6.7×10^{-4}. This value is in good agreement with the results obtained below (cf. Table III).

The recent theories of polymer solutions made it possible to estimate both the unperturbed dimensions and the excluded volume effect from the data in any solvent, good or

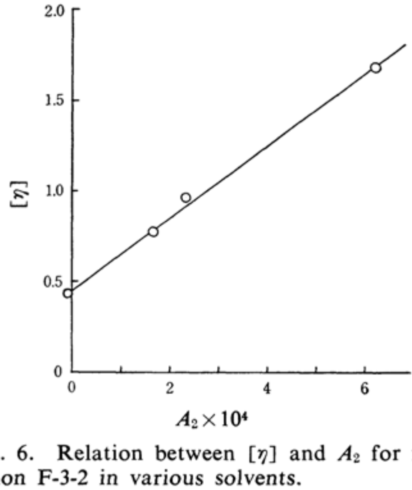

Fig. 6. Relation between $[\eta]$ and A_2 for fraction F-3-2 in various solvents.

---

[11] P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).

[12] W. R. Krigbaum, *J. Polymer Sci.*, **18**, 315 (1955).

TABLE III. COMPARISON OF UNPERTURBED MOLECULAR PARAMETERS OF VARIOUS POLYMERS

Polymer	Temp. °C	$K_0 \times 10^4$	$(\overline{R}^2_0/M)^{1/2}$ $\times 10^{11}$	$(\overline{R}^2_{0f}/M)^{1/2}$ $\times 10^{11}$	$(\overline{R}^2_0/\overline{R}^2_{0f})^{1/2}$	Ref.
PMVP	25	6.9±0.5 from Eq. 8 7.0±0.5 from Eq. 11	652±15	282	2.31±0.05	Present work
Poly-4-vinylpyridine	25	8.1	686	301	2.28	1
Poly-2-vinylpyridine	25	7.9	680	301	2.26	14
Polystyrene	34	8.2	688	302	2.28	15

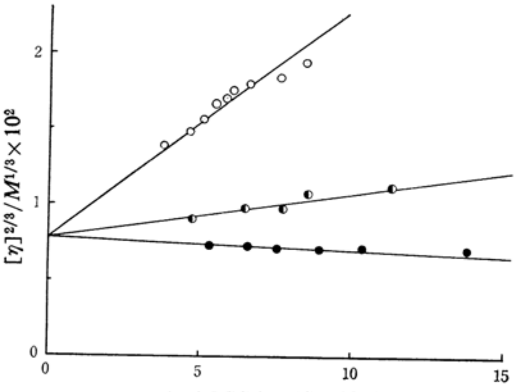

Fig. 7. $g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}$ vs. $[\eta]^{2/3}/M^{1/3}$ for PMVP.
-○-: Methanol -◐-: MEK
-●-: Toluene

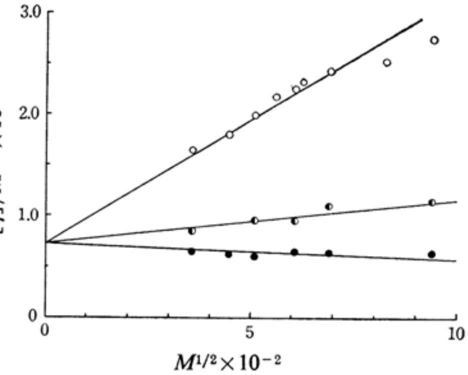

Fig. 8. $[\eta]/M^{1/2}$ vs. $M^{1/2}$ for PMVP.
-○-: Methanol
-◐-: MEK
-●-: Toluene

poor. According to the theory of Kurata-Stockmayer-Roig,4)

$$[\eta]^{2/3}/M^{1/3} = K_0^{2/3} + 0.363\Phi_0 B[g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}] \quad (8)$$

$$g(\alpha_\eta) = 8\alpha_\eta^3/(3\alpha_\eta^2+1)^{3/2} \quad (9)$$

where

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \quad (10)$$

and where B is the parameter of the excluded volume effect. Figure 7 shows the plots of $[\eta]^{2/3}/M^{1/3}$ against $g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}$ as obtained in the usual manner.13)

Very recently Stockmayer and Fixman5) proposed the following equation:

$$[\eta]M^{1/2} = K_0 + 0.51\Phi_0 BM^{1/2} \quad (11)$$

where K_0 is the intercept of the plots of $[\eta]/M^{1/2}$ against $M^{1/2}$. The plots are shown in Fig. 8. The K_0 values obtained by both Eqs. 8 and 11 are in close agreement, and using the average value the unperturbed molecular parameters were calculated. The results are shown in Table III, together with those of other vinylpyridine polymers and polystyrene.

The quantity $(\overline{R}_0^2/\overline{R}^2_{0f})^{1/2}$ may be used as a measure of the extension of the polymer chain. Here $\overline{R}^2_{0f}$ is the unperturbed mean square end-to-end distance in the absence of any hindrance about each single bond; its value was calculated by assuming a C–C bond length to be 1.54 Å and the tetrahedral angle to be 109.5°.

As is shown in Table III, the value of $(\overline{R}^2_0/\overline{R}^2_{0f})^{1/2}$ for PMVP is slightly higher than the values for the other polymers, but the difference is within the range of experimental error. Thus, it can be concluded that the degree of the extension of PMVP is almost the same as those of the other polymers. This is perhaps to be expected from the fact that the methyl substituent of PMVP is relatively small in size and is located at the farthest position with regard to the carbon atom of the main chain. Therefore, the methyl group may make only a minor contribution to the internal rotation about the C–C bonds of the polymer chain.

Summary

Nine fractionated samples of poly-2-methyl-5-vinylpyridine (PMVP) have been investigated by viscosity and light-scattering measurements at 25°C. In the range of the molecular weights from about 1×10^5 to 1×10^6, the following relationship between the intrinsic viscosity and

---

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

14) S. Arichi, private communication.

15) W. R. Krigbaum and P. J. Flory, *J. Polymer Sci.*, 11, 37 (1953).

the molecular weight in methanol has been obtained: $[\eta]=0.80\times10^{-4}M_w^{0.76}$. The unperturbed molecular dimensions have been obtained using the recent theories of the solution behavior of high polymers. The results have been compared with those of other vinylpyridine polymers and polystyrene, and it has been found that the degree of the extension of PMVP is almost the same as those of the other polymers.

The authors wish to express their thanks to Mr. Shizuo Arichi of this University for his helpful discussions throughout this work. They also wish to thank the Institute of Takeda Yakuhin Co. for making the elementary analysis.

Department of Chemistry
Faculty of Science
Hiroshima University
Hiroshima