Mem. Fac. Lit. & Sci., Shimane Univ., Nat. Sci., **3**, pp. 69—77, 7 text-figs., 3 tables, March, 20, 1970

Viscometric Studies of Poly-2-methyl-5-vinylpyridine in Dilute Solutions

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(Received November 29, 1969)

INTRODUCTION

The solution properties of poly-2-methyl-5-vinylpyridine have been reported by H. Sato et al.[1)], M. Miura et al. [2)] and G. B. Gechele et al. [3)] . Molecular parameters such as Flory constant, K_θ , steric factor, σ, Mark-Houwink-Sakurada constants, K' and α, and entropy parameter, ψ, in some solvents were determined in these papers. Nevertheless, it is meaningful to estimate these parameters in more solvents and by a new method if it is possible.

In particular, estimation of Mark-Houwink-Sakurada equations in as many solvents as possible will make it more favorable to determine molecular weight of this polymer from viscosity measurement. In this paper, data of viscosity of poly-2-methyl-5-vinylpyridine in seven solvents and of molecular weights for seven fractions were analyzed with usual methods. A new method for determination of Flory constant proposed by S. Gundiah [4)] was also investigated in this paper.

EXPERIMENTAL

Materials

Poly-2-methyl-5-vinylpyridine Poly-2-methyl-5-vinylpyridine fractions were kindly supplyed from Prof. M. Miura of Hiroshima University. Details concerning polymerization and fractionation of these fractions used in this study were described in his paper [2)].

Solvents Solvents used in this study were constant-boiling fractions of special grade methyl ethyl ketone(MEK), dimethylformamide(DMF), tetrahydrofuran(THF), pyridine, chloroform, methanol and isopropanol. These solvents were distilled immediately before use with two 100-cm. jacketed columns containing Podvielniak single turn helix packing which were constructed in our laboratory.

Viscosity Viscosity measurements were carried out with five modified Ubbelohde-type viscometers in thermobath controlled to 30° ± 0.01°C. The flow time of solvent was more than 100 sec. per 2.0 ml. of efflux volume according to the viscometer used and the corrections of kinetic energy and rate of shear were negligible. All solutions were prepared with heating at about 60°C for an hour to dissolve solutes perfectly and then were filtered through a No.3 sintered glass filter immediately before measurement. The concentration of solutions was determined by a weighing method.

Light Scattering Light scattering of dilute polymer solutions for determination of the weight-average molecular weight, M_w, was measured with a Brice-type Shimadzu-PG-21 photometer at 25° ± 0.1°C. Solutions were clarified with care through double sheets of Sartorius membrane filter "Cellafilter, mittel". Scatterings were measured with vertically polarized incident light of 436 mμ and the vertical components of scattered light were analyzed and correction of anisotropy [5] was made. Correction for back reflection was also made using the value of r_F 0.088[6]. The instrumental constant was determined by assuming that R_{90} for benzene at 25°C is 48.5×10^{-6} for unpolarized light of 436 mμ [7].

The value of the incremental refractive index dn/dc for polymer solutions at 436 mμ was determined using Shimadzu DR-3 type differential refractometer. The value of dn/dc for polymer solution in methanol containing 0.02N-NH_3 was 0.285 at 25°C. The scatterings of polymer solution at four concentrations and of a solvent were determined for eleven angles between 30° and 150°.

RESULTS and DISCUSSION

The data of light scattering were analyzed in the manner proposed by Zimm [8]. For random coils, the equation of light scattering is as follows:

$$\begin{aligned} Kc/R_\theta &= 1/M_w P(\theta) + 2A_2 c \\ &= (1/M_w)\,(1+16\pi^2/3\lambda^2)\,R_G^2\ \sin^2(\theta/2) + 2A_2 c \end{aligned} \tag{1}$$

where R_θ is the Rayleigh ratio measured at an angle of θ to the incident beam, M_w is the weight-average molecular weight of the scattering solute, $P(\theta)$ is the particle scattering factor, $R_G{}^2$ is the mean square radius of gyration, A_2 is the second virial coefficient for the system under study, c is the concentration in grams per milliliter, and

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

for vertically polarized incident light of wave length, λ. In the equation above, n_0 is the refractive index of the solvent, dn/dc is the rate of change of refractive index of the solution with concentration, N_A is Avogadro's number.

According to equation (1), M_w is obtained from the intercept of the plot of Kc/R_θ against kc + $\sin^2(\theta/2)$, where k is an arbitrary constant. A typical example of the Zimm plot for a fracion of poly-2-methyl-5-vinylpyridine, fratction V-1, in methanol containing 0.02N-NH_3 is shown in Fig. 1. Ammonia was added to methanol in order to suppress any ionization of pyridine nitrogen of the polymer [2,9]. The results of molecular weight determination by the light scattering are summarized in Table I.

It has been generally recognized that the relation between η_{sp}/c and c, and that between ln η_r/c and c are represented by the Huggins' equation[10] and Kraemer's one [11] as follows:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \tag{2}$$

$$\ln\ \eta_r/c = [\eta] - k''[\eta]^2 c \tag{3}$$

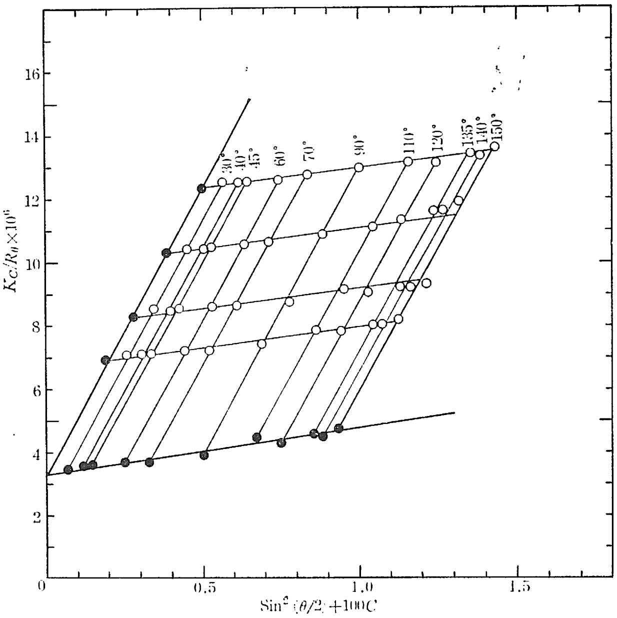

Fig. 1. The Zimm plots of fraction V-1 in methanol -0.02N NH_3 solution at 25°C.

Table I. The results of the weight-average molecular weights and unperturbed viscosity data of each fraction of poly-2-methyl-5-vinylpyridine.

Fraction	$M_w \times 10^{-5}$	$[\eta]_R$	Fraction	$M_w \times 10^{-5}$	$[\eta]_R$
I − 2	61.0	0.69	V − 3	36.3	—
II − 1	52.2	0.63	V − 1	30.5	0.48
III − 1	42.3	0.56	VI − 1	25.8	0.42
III − 3	39.2	0.54			

where η_r , η_{sp} and $[\eta]$ are the relative viscosity, the specific viscosity and the limiting viscosity number, respectively ; k', the Huggins' constant, and k'', the Kraemer's slope constant. It is said that k' and k'' are constants independent of the molecular weight of polymer but depend on the property of solvent and temperature.

Results of viscosity measurement in pyridine solution as a typical example are plotted according to equations (2) and (3) in Fig. 2, and then k' and k'' vs. $[\eta]$ plots in the same case are shown in Fig. 3. The values of $[\eta]$, and k'' $[\eta]^2$ were obtained by the method of least squares and summarized in Table II.

For any given fraction, $[\eta]$ varies with the solvent, the order of values generally being MEK $<$ DMF $<$ THF $<$ pyridine $<$ chloroform $\leqq$ methanol $\leqq$ isopropanol. It is clear that the polarity of the solvent affects strongly the limiting viscosity number in this polymer-solvent system : $[\eta]$ is smaller in the basic solvent and larger in the acidic. The interactions between nitrogen atoms in the side chain and the solvent molecules seem to determine the expansion of polymeric coil in the solution. For example, the hydrogen bonding between nitrogen atoms and hydroxyl groups of

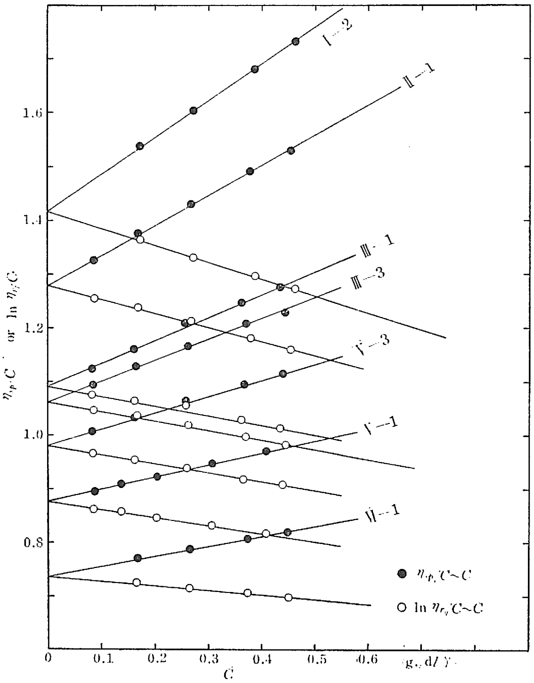

Fig. 2. Viscosity-concentration plots for poly-2-methyl-5-vinylpyridine in pyridine solution at 30° ±0.01°C.

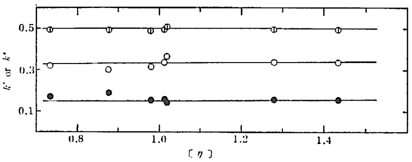

Fig. 3. Plots of Huggins' constant k' (○) and Kraemer's slope constant k'' (●) vs. intrinsic viscosity of poly-2-methyl-5-vinyl-pyridine in pyridine solution at 30°C. (⊖) : $k'+k''$

Table II. Viscosity data for poly-2-methyl-5-vinylpyridine in various solvents at 30° ± 0.01°C

Fraction	Isopropanol		Methanol		Chloroform		Pyridine		Tetrahydro furan		Dimethyl formamide		Methyl ethyl ketone	
	$[\eta]$	$k''[\eta]^2$	$[\eta]$	$k''[\eta]^2$	$[\eta]$	$k''[\eta]^2$	$[\eta]$	$k''[\eta]^2$	$[\eta]$	$k''[\eta]^2$	$[\eta]$	$k''[\eta]^2$	$[\eta]$	$k''[\eta]^2$
I − 2	1.986	0.603	1.961	0.570	1.929	0.511	1.417	0.312	1.268	0.232	1.112	0.193	1.961	0.570
II − 1	1.796	0.540	1.750	0.429	1.811	0.501	1.279	0.257	1.151	0.193	1.004	0.144	1.750	0.429
III − 1	1.519	0.387	1.479	0.321	1.445	0.295	1.090	0.167	1.963	0.164	1.867	0.120	1.479	0.321
III − 3	1.444	0.382	1.409	0.311	1.397	0.279	1.062	0.176	1.912	0.122	1.801	0.114	1.409	0.311
V − 3							0.980	0.165			0.749	0.087		
V − 1	1.190	0.253	1.183	0.202	1.167	0.187	0.876	0.145	0.773	0.103			1.183	0.202
VI − 1	1.019	0.144	1.008	0.091	1.035	0.144	0.733	0.092	0.669	0.058	0.622	0.094	1.008	0.091

alcohols will cause the solvation of alcohol molecules and therefore coil will expand.

Figure 4 shows plots of log $[\eta]$ against log M_w at 30°C for each solvent. Points are on the straight lines and the constants K' and α in Mark-Houwink-Sakurada equation were summarized in Table III. As a rule, the value of the exponent, α, may be regarded as a measure of chain extension and the order of variation of α with solvents coincides with that of $[\eta]$ with solvents for any given fraction. From this we concluded that alcohols are good solvents and ketone and amide which are basic, are poor solvents. The order of goodness of the solvent in this polymer-solvent system was

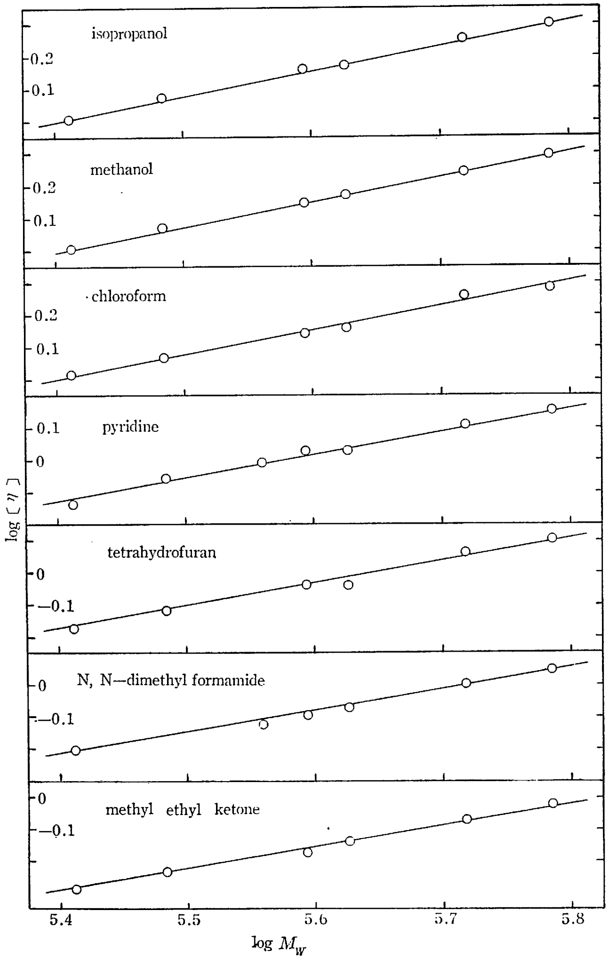

Fig. 4. Plots of log [η] vs. log M_w of poly-2-methyl-5-vinylpyridine in various solvents at 30°C.

Table III. Constants K' and α of Mark-Houwink-Sakurada equation of Poly-2-methyl-5-vinylpyridine in various solvents.

Solvent	$K'\times10^4$	α
MEK	1.14	0.66
DMF	1.48	0.67
THF	1.12	0.70
pyridine	1.10	0.71
chloroform	0.79	0.76
methanol	0.60	0.78
isopropanol	0.61	0.78

the same with those reported in poly-2-vinylpyridine 12) and poly-4-vinylpyridine-solvent systems 13) .

According to the recent theories of polymer solution 14, 15, 16) the short range and long range interaction parameters of polymer molecules in dilute solution may be obtained from viscosity data.

The equation proposed by Stockmayer and Fixman 13) is as follows :

$$[\eta]/M^{1/2}=K_\theta+0.51\,\Phi_0 BM^{1/2} \qquad (4)$$

where K_θ is the short range interaction parameter and expressed as

$$K_\theta=\Phi_0(L_0^2/M)^{3/2} \qquad (5)$$

where Φ_0 is the universal constant whose value is 2.87×10^{21} (for homogeneous polymers) and L_0^2 is the mean square end-to-end distance at unperturbed state, and B is the long range interaction parameter.

The values of $[\eta]/M_w^{1/2}$ and $M_w^{1/2}$ are plotted according to equation (4) in Fig. 5. The lines for viscosities in all solvents pass through the same intercept and are linear as expected from equation (4). Hence the value K_θ was obtained from the intercept as 7.2×10^{-4}. The order of the values of B which are comparable to the tangent of the lines for each solvent agrees with that of the exponents α in the Mark-Houwink-Sakurada's equations.

Recently Gundiah et al. 4, 17, 19, 20) have proposed a new method of estimation of the value of K_θ. According to the method, when the viscosity functions $\ln \eta_r/c$ are plotted against concentrations of solutions for a particular polymer in different solvents, the value of the ordinate at the common point of intersection gives $[\eta]_R$, which is

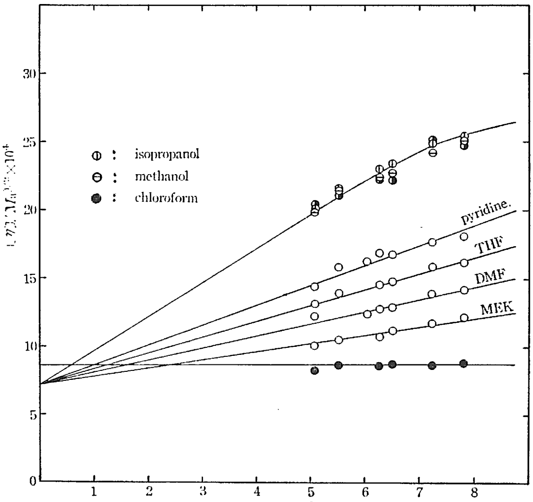

Fig. 5. Plots of $[\eta]/M_w^{1/2}$ vs. $M_w^{1/2}$ for poly -2-methyl-5-vinyl-pyridine at 30°C.
(●) : $[\eta]_R/M_w^{1/2} \sim M_w^{1/2}$ plot.

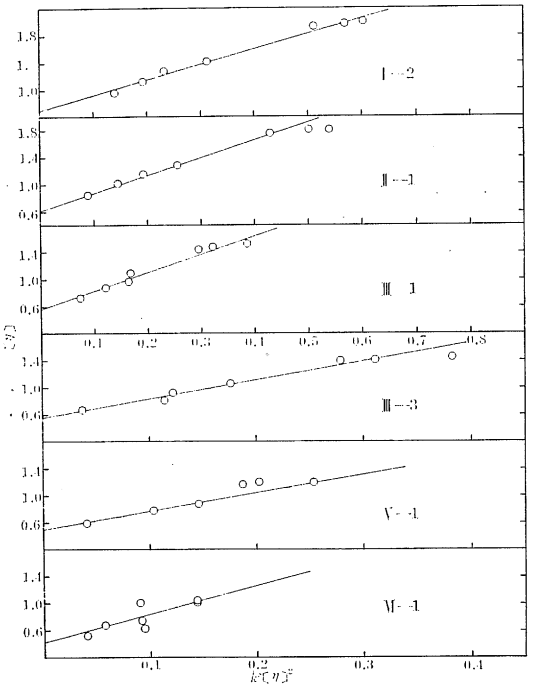

Fig. 6. Plots of the limiting viscosity number vs. the slope of the viscosity-concentration plot for poly-2-methyl-5-vinylpyridine.

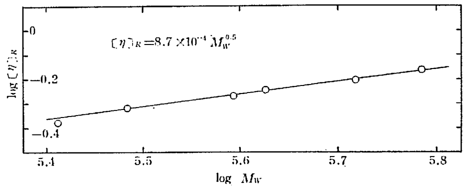

Fig. 7. $[\eta]_R$-molecular weight relation for poly-2-methyl-5-vinyl-pyridine.

related to the molecular weight by

$$[\eta]_R = K'M^{1/2} \tag{6}$$

Gundiah did point out that K' in equation (6) is nearly equal to K_θ in equations (4) and (5). In Fig. 6, $[\eta]$ is plotted against k'' $[\eta]^2$. Points are on the straight line and therefore an important assumption used by Gundiah seems to be satisfied in this polymer-solvent system. The values of $[\eta]_R$ are obtained from the intercepts of ordinate of Fig. 6, which are summarized in Table I. In Fig. 7, log $[\eta]_R$ is plotted against log M_w. The slope of the straight line is almost 1/2 and K' is obtained to be 8.7×10^{-4} which is a little larger than that obtained from Fixman's plot. $[\eta]_R/M^{1/2}-M^{1/2}$ plots are also shown together in Fig. 5.

The value of K_θ obtained above must be corrected for molecular weight distribution of polymer. The correction can be carried out by the following equation[18].

$$K_{\theta 0} = K_\theta q_w$$

where $K_{\theta 0}$ is the corrected value of K_θ and q_w is the correction factor which is obtained by

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

where M_n is the number-average molecular weight. Unfortunately, the values of M_n for any fraction were not measured in this study.

However, it may be assumed that M_w/M_n is about 2 in consideration of preparation of polymer fractions. If we take the value of 2, q_w is 0.94 and therefore $K_{\theta 0}$ is 7.7× 10^{-4} for K_θ obtained by Fixman's method and 9.2×10^{-4} for that obtained by Gundiah's. The former is a little smaller than the value obtained by Gechele et al.[3], $(8.4 \pm 0.5)\times10^{-4}$ and is a little larger than that by Miura et al.[2], $(7.0 \pm 0.5)\times10^{-4}$. The value of $K_{\iota 0}$ obtained from $[\eta]_R$ method is somewhat larger than any other values.

In the case of polymethyl methacrylate, Gundiah et al.[20] concluded that the higher value of K_θ obtained by $[\eta]_R$ method is perhaps due to influence of the microstructure on the unperturbed dimensions of the polymeric chains. But, the accumulation of more data is necessary to decide whether the higher value in this study is in the case.

As a measure of the hindrance to the internal rotation around the main chain of a linear polymer, the steric factor, σ, is defined by[16]

$$L_0^2/L_{0f}^2 = \sigma^2 \qquad (7)$$

where L_{0f} is the unperturbed mean square end-to-end distance of freely rotated chain. Using the value of $K_{\theta 0} = 7.7\times10^{-4}$, the value of $(L_0^2/M)^{1/2}$ for poly-2-methyl-5-vinylpyridine was calculated to be 644×10^{-11} at 30°C by equation (5). $(L_{0f}^2/M)^{1/2}$ was found to be 282×10^{-11} by assuming the C-C bond length and tetrahedral angle to be 1.54 A, 109.5° respectively. The value of σ was calculated by equation (7) to be 2.28 at 30° C, which is in the range of appropriate values reported, 2.31 at 25°C for this polymer[2] and 2.24 and 2.37 for analogous polymers, poly-2-vinylpyridine[18] and poly-4-vinylpyridine[16], respectively. Therefore, it may be concluded from these data that the methyl substituent of this polymer compared with the analogous polymers, and/or the difference of temperature (5°C) do not affect the steric hindrance of the internal rotation around the main chain remarkably.

SUMMARY

The viscosities of a series of seven fractions of poly-2-methyl-5-vinylpyridine in methyl ethyl ketone, dimethylformamide, tetrahydrofuran, pyridine, chloroform, methanol, and isopropanol and also molecular weights of several fractions were determined.

The Mark-Houwink-Sakurada equations were determined as follows at 30°C :

$[\eta] = 1.14\times10^{-4}\ M_w^{0.66}$ in MEK
$[\eta] = 1.48\times10^{-4}\ M_w^{0.67}$ in DMF
$[\eta] = 1.12\times10^{-4}\ M_w^{0.70}$ in THF
$[\eta] = 1.10\times10^{-4}\ M_w^{0.71}$ in pyridine
$[\eta] = 0.79\times10^{-4}\ M_w^{0.76}$ in chloroform
$[\eta] = 0.60\times10^{-4}\ M_w^{0.78}$ in methanol
$[\eta] = 0.61\times10^{-4}\ M_w^{0\ 78}$ in isopropanol

The Flory constant, K_θ, in the equation, $[\eta]_\theta = K_\theta M^{1/2}$, was determined by the Fixman's method to be 7.7×10^{-4}. The steric factor, σ, was 2.28 which agrees with those reported for this polymer, poly-2-vinylpyridine and poly-4-vinylpyridine.

Application of new $[\eta]_R$ method proposed by Gundiah et al. was also tried to this polymer. And the value of K_θ obtained was 9.2×10^{-4}, which was a little larger than those described above.

The author wishes to express his thanks to Prof. Masaji Miura of Hiroshima University for furnishing the materials and his encouragement in this work, and to A. Prof. Kenji Toki of this University for making this study possible and for his kind advice.

Particular thanks are also due to Dr. Shizuo Arichi of Kumamoto University for permiting the author to measure the light scattering and for his many valuable advices and discussions throughout this work.

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