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Solution Properties of Low Molecular Weight Fractions of Poly(2-vinylpyridine)

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The relationships between the weight-average molecular weight M_w and the intrinsic viscosity $[\eta]$ of poly(2-vinylpyridine) [P2VP] in benzene and methyl alcohol at 25 °C, were investigated by the use of fractions with molecular weights ranging from 2.1×10^3 to 2.3×10^4. The exponent ν in the Mark-Houwink-Sakurada equation, $[\eta]=K_0M_w^{\nu}$, was 0.5 in both solvents when M_w was lower than about 10^4. A constant K_0 was approximately in accord with Flory's K_θ value for ordinary high-molecular-weight P2VP, obtained earlier in respective solvents. By measuring $[\eta]$ for these low-molecular-weight fractions in several solvents at different temperatures, the temperature coefficients of an unperturbed dimension, $d\ln\bar{r}^2_0/dT$, of this polymer were estimated and averaged to be $-2.3\times10^{-3}\,K^{-1}$. These are quite different from the positive values calculated from the K_θ's by Dondos *et al.* which were estimated using the extrapolation method for non-θ-solvents. Our results were further corroborated after adding a K_θ value which was directly determined at another θ-state; *i.e.* in toluene at 63.7 °C, to that in benzene at 16.2 °C published earlier, which was found from phase-separation experiments in this work.

Extensive theoretical and experimental investigations regarding the temperature coefficient of the unperturbed dimension, $d\ln\bar{r}^2_0/dT$, have been made for linear polymers because they offer important information on the hindrance potential affecting rotation around bonds in the main chain.[1] The value of $d\ln\bar{r}^2_0/dT$ can be evaluated by measuring the stress-temperature coefficient for a cross-linked network,[2] or more directly by measuring the unperturbed mean-square end-to-end dimension,[3] $\bar{r}^2_0$, or the intrinsic viscosity,[4] $[\eta]_\theta$ in several θ-solvents with different θ-temperatures distributed within a certain temperature range. Naturally, the Stockmayer-Fixman plot, as an indirect method, is frequently used to evaluate $d\ln\bar{r}^2_0/dT$, for Flory's K_θ values can be calculated from the $[\eta]$ values for different molecular-weight fractions in non-θ-solvents at several temperatures.[5,6] Flory *et al.* also proposed a method in which the temperature coefficient of $[\eta]$ of linear polymer is measured in athermal solvents.[7,8]

In general, it is often impossible to find the θ-solvent and/or θ-temperature for some polymers, since the elimination of the long-range interactions of a polymer in non-θ-solvent is troublesome, especially for polar polymers.[9] The method proposed by Bianchi *et al.* is effective in such cases.[9—11] According to them, the coil-expansion factor α, is essentially unity in many solvents when the molecular weight of the polymer is sufficiently low. Consequently, the temperature coefficient of the intrinsic viscosity of such low-molecular-weight fraction is equal to that of the unperturbed dimension. As for poly(2-vinylpyridine), P2VP, it is very difficult to determine a single component θ-solvent. Only values for benzene have been reported; 16.2 °C or 15 °C for this polymer.[12,13] Most of the reported values for the unperturbed dimension of P2VP were evaluated in non-θ-solvents and at very limited temperatures. In addition, even the sign of the temperature coefficients of the unperturbed dimension estimated from these literature values differs with each other.

The main purpose of this study was to determine the $d\ln\bar{r}^2_0/dT$ of P2VP according to the method of Bianchi *et al.* Moreover, the experimental evidence supporting the results was complementarily shown by the estimation of $d\ln\bar{r}^2_0/dT$ using the K_θ values which were directly observed in θ-solvents, benzene and toluene. The latter was proved to be a θ-solvent at 63.7 °C.

Experimental

The monomer of 2-vinylpyridine was kindly supplied by Tokyo Yukigosei Co., and was distilled under a reduced pressure (bp 55 °C/15 Torr (1 Torr=133.322 Pa)) immediately before use. Polymerization was carried out either by the anionic method (Samples denoted below by BL and C) using butyllithium in tetrahydrofuran(THF) under a reduced pressure at −27 °C, or by the radical method (Samples denoted by A) with azobisisobutyronitrile in benzene at 50 °C. Fractionation of the polymer was carried out by the successive precipitation method using benzene and hexane as a solvent-precipitant pair, as outlined elsewhere.[14]

The phase separation was carried out in a thick glass capillary tube as described by Cowie *et al.*[15] After being measured with modified Ubbelohde-type dilution viscometers in a water bath (thermostatically controlled within ±0.01 °C), the intrinsic viscosity $[\eta]$ was calculated in dl/g with the Huggins plot.

Light scattering was carried out with a Fica 50 automatic light-scattering photometer with vertically polarized incident light of 436 nm. The vertically polarized component of the scattered light was measured for scattering angles of 30°—150° in methyl alcohol at 25 °C. The optical purification of each solution and solvent was achieved by filtration

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Table 1. Light-scattering and viscosity data for poly(2-vinylpyridine) at 25 °C

Fraction	$M_w \times 10^{-3}$	[η] MeOH	[η] Benzene	d*n*/d*c* MeOH
BL6-2	22.9	0.170	0.111	0.263
BL6-3	13.1	0.117	0.089	0.262
BL6-4	9.4_6	0.099	0.075	—
BL6-5	7.4_9	0.086	0.065	0.261
BL6-6	5.4_6	0.074	0.057	—
BL6-7	4.9_5	0.073	0.055	0.262
BL6-8	3.5_5	0.057	0.043	—
BL6-9	2.1_0	0.043	0.039	0.259

through Millipore membrane filters "FG"(pore size: 0.2 μm). An antifluorescence filter of 436 nm was also used to remove the effect of the fluorescence which was confirmed not to be negligible. The weight-average molecular weight M_w was calculated using the double-extrapolation plots of Zimm.

The specific refractive-index increment d*n*/d*c* was measured in methyl alcohol at 25 °C with a Shimadzu DR-3 type refractometer.

Results and Discussion

Table 1 summarizes the [η] results obtained in methyl alcohol and benzene and, also, those of M_w and d*n*/d*c* in methyl alcohol (all measured at 25 °C for the low-molecular-weight fractions of P2VP).

Concerning the molecular weight dependence of d*n*/d*c*, Kamata *et al.*[16] found considerable fluctuations for oligostyrene in an ethyl methyl ketone when the molecular weight was lower than 2000. As can be seen in Table 1, d*n*/d*c* for P2VP is essentially in accordance with each other for all the fractions measured in this study. Also, the average value of 0.262 is close to that of 0.270, reported for ordinary high-molecular-weight P2VP fractions in the same solvent.[17] Therefore, the value of 0.262 was used in the calculation of M_w from light-scattering data in this study.

In Figs. 1 and 2, the [η]'s for methyl alcohol and benzene are plotted against M_w, respectively. The points for the ordinary high-molecular-weight P2VP fractions (reported by one of the authors[12]) are represented by filled circles for comparison. As can be seen in both Figs., the points can be represented by two distinct straight lines. These are the so-called Mark-Houwink-Sakurada empirical equation:

$$[\eta] = KM_w^{\nu}, \tag{1}$$

where *K* and *ν* are constants. The point for the fraction BL6-2 in methyl alcohol, for example, is on the line for the higher molecular-weight fractions, however, the remaining points are on a different straight line. Using a least-squares method, the constants K_0 and *ν* of the lines for the lower-molecular-weight fractions were determined as follows:

$$[\eta] = 10.0 \times 10^{-4} M_w^{0.5} \quad \text{in methyl alcohol,} \tag{2}$$

$$[\eta] = 7.5 \times 10^{-4} M_w^{0.5} \quad \text{in benzene.} \tag{3}$$

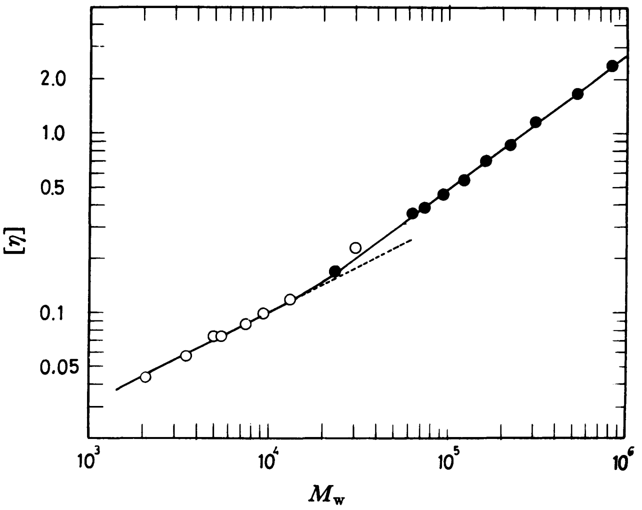

Fig. 1. Double logarithmic plot of [η] against M_w for poly(2-vinylpyridine) in methyl alcohol at 25 °C. Filled circles represent the relationship obtained earlier.[12]

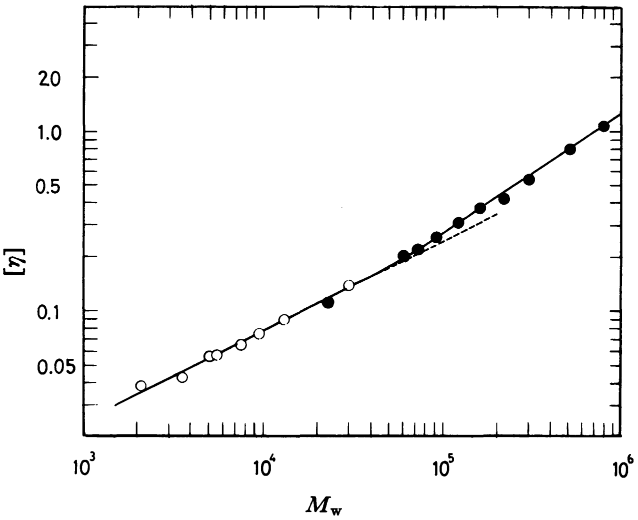

Fig. 2. Double logarithmic plot of [η] against M_w for poly(2-vinylpyridine) in benzene at 25 °C. Filled circles represent the relationship obtained earlier.[12]

The breaks for these two lines in Figs. 1 and 2 occur in the vicinity of $M_w \approx 1.5 \times 10^4$ in methyl alcohol, and 4×10^4 in benzene, respectively. The existence of such breaks has been reported for many polymers.[11,18–21] Hirai *et al.*[22] reported two distinct sections in log[η]—logM_n plots for poly(4-vinylpyridine) fractions in *t*-butyl alcohol, methyl alcohol, and ethyl methyl ketone–isopropyl alcohol mixture (85:15 by wt.) at 30 °C, where M_n is the number-average molecular weight. They also found that the slope of the lines is 0.5 for all solvents in the region of molecular weight below 10^4.

According to Bianchi *et al.*,[10,11,23,24] when the molecular weight is sufficiently low, there is a molecular-weight range for many polymers where the expansion coefficient α is practically undistinguishable from unity. Hence, the K_0 constant of the Mark-Houwink-Sakurada equation in such a molecular-weight range is almost equal to K_θ, which is defined as follows:

$$[\eta]_\theta = K_\theta M^{1/2}, \quad (4)$$

$$K_\theta = \Phi_0(\bar{r}^2_0/M)^{3/2}. \quad (5)$$

Φ_0 is Flory's viscosity constant, and M is the polymer molecular weight. It is, therefore, interesting to compare the K_0 values in Eqs. 2 and 3 with K_θ reported in the literature for each corresponding P2VP-solvent system at 25 °C. In fact, the above-mentioned values of $K_0=10.0\times10^{-4}$ in methyl alcohol and 7.5×10^{-4} in benzene agreed fairly well with those of $K_\theta=9.3\times10^{-4}$ and 7.9×10^{-4} in each solvent, derived from the Stockmayer-Fixman plot by one of the authors.[12]

From these results, it may be concluded that when the molecular weight of P2VP is lower than *ca.* 1×10^4 at least, the excluded volume effect can be considered negligible even in a very good solvent such as methyl alcohol. This was similarly reported for many other linear polymers. Thus, we can evaluate $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ by measuring the temperature coefficient of $[\eta]$ in any solvent with a low molecular-weight fraction by means of the following equation:

$$\mathrm{dln}\,\bar{r}^2_0/\mathrm{d}T = (2/3)\mathrm{dln}\,[\eta]/\mathrm{d}T. \quad (6)$$

The intrinsic viscosities for P2VP fractions, BL6-7 ($M_w=4.9_5\times10^3$) and Al-V ($M_w=7.8_7\times10^3$) were measured in ethyl alcohol, chloroform, dioxane, THF, ethyl methyl ketone, and benzene in the temperature range of 14.9° to 60 °C. In Figs. 3 and 4, the ln[η] for the above two fractions was plotted against temperature, respectively. All plotted points fall on straight

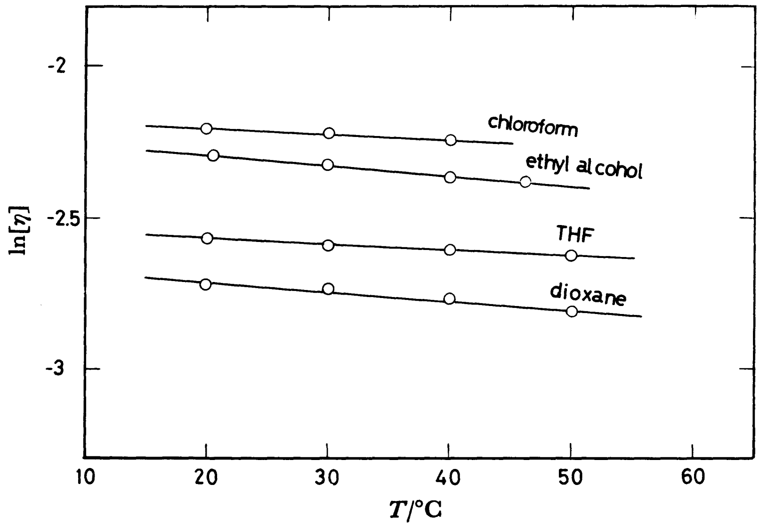

Fig. 3. Plots of ln[η] *vs.* temperature for poly(2-vinylpyridine) fraction A-1-V in various solvents.

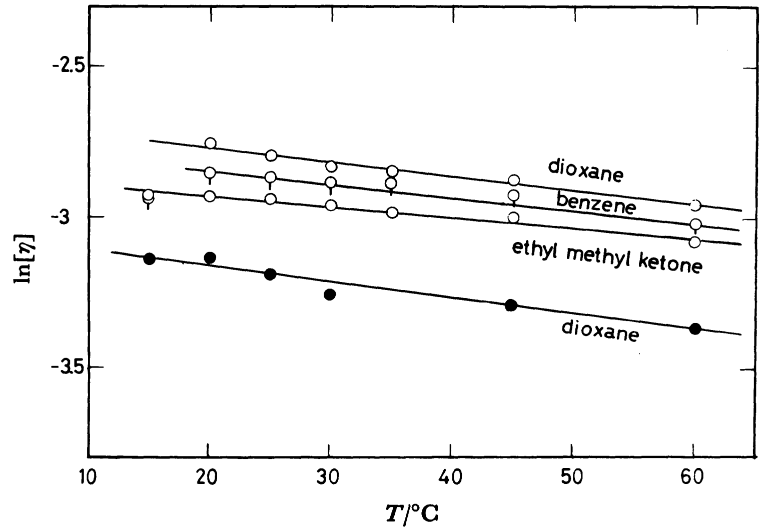

Fig. 4. Plots of ln[η] *vs.* temperature for poly(2-vinylpyridine) fractions BL6-7 (○) and BL6-9 (●) in various solvents.

TABLE 2. TEMPERATURE COEFFICIENT OF UNPERTURBED DIMENSION OF POLY(2-VINYLPYRIDINE) ESTIMATED FROM INTRINSIC VISCOSITY IN VARIOUS SOLVENTS

Fraction	$M_w\times10^{-3}$	Solvent	$[\mathrm{dln}\,\bar{r}^2_0/\mathrm{d}T]\times10^3$ This work	Lit,[25,26]
A-1-V	7.8_7	Ethyl alcohol	−2.4	0.6
A-1-V	7.8_7	Chloroform	−1.2	−0.2
A-1-V	7.8_7	Dioxane	−1.9	—
A-1-V	7.8_7	Tetrahydrofuran	−1.2	6.7
BL6-7	4.9_5	Dioxane	−3.0	—
BL6-7	4.9_5	Ethyl methyl ketone	−2.6	—
BL6-7	4.9_5	Benzene	−2.4	3.4
BL6-9	2.1_0	Dioxane	−3.4	—
—	—	Methyl alcohol	—	4.3
—	—	Isopropyl alcohol	—	2.6
—	—	Cyclohexanol	—	1.8

lines for each solvent except the one at 14.9 °C in benzene. This deviation may be explained by the fact that a temperature of 14.9 °C is slightly lower than the θ-temperature, 16.2 °C for the P2VP–benzene system.[12]

The temperature coefficients of $\mathrm{dln}[\eta]/\mathrm{d}T$ were analyzed by a least-squares method, and the values of $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ were calculated according to Eq. 6 and are summarized in Table 2. As shown in the Table, the values of $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ estimated in this study were explicitly negative for all solvents used and were averaged to be $-2.3(\pm1.1)\times10^{-3}\,\mathrm{K}^{-1}$. Concerning those of P2VP, there has been no value in the literature except for the data on K_θ obtained at only two or three different temperatures. Our estimated values of $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ from such data on K_θ reported by Dondos *et al.*[13,25,26] are cited in the last column of Table 2. Though a practical estimation of these values is indeed a delicate problem, it is noted that even the signs of $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ (for the latter) are reverse to those obtained in this work (except in chloroform). This may, perhaps, be due to the inevitable ambiguity in the K_θ values of Dondos *et al.*, which were indirectly determined in non-θ-solvents with an extrapolation method based on the two-parameter theory for dilute polymer solutions.

Strictly, it will be better, therefore, to estimate $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ from the K_θ obtained for an ordinary high-molecular-weight polymer in more than two single θ-solvents with different θ-temperatures. One of us has reported that benzene is the θ-solvent for P2VP at 16.2 °C and that the value of K_θ directly deduced by measuring the viscosity at the state is 9.1×10^{-4} (after a correction due to the molecular-weight heterogeneity in samples)[12] is different from the above-quoted value indirectly determined at 25 °C. However, no other single θ-solvent has been reported. We did find in this investigation that toluene is expectative. As is well known, the unperturbed dimension of a linear polymer is often affected by the specific solvent effect, but benzene and toluene are homologous nonpolar solvents and the specific solvent effect on the unperturbed dimension of P2VP is considered to be the same and not so large. Hence, an estimation of $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ from K_θ for these solvents will be useful.

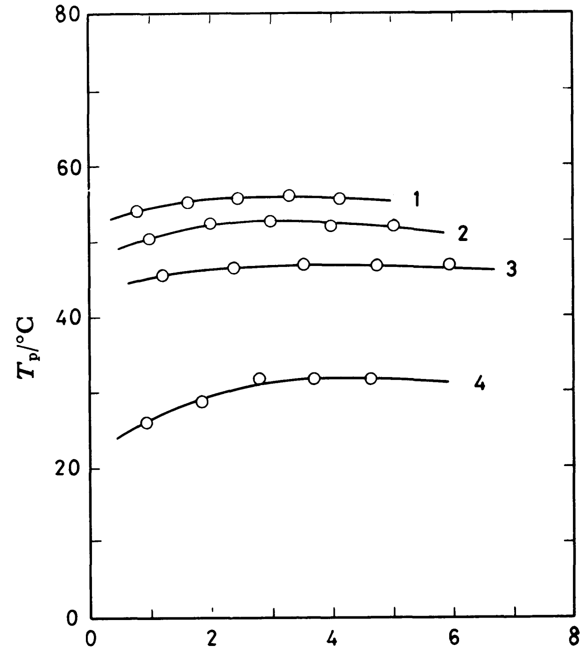

Fig. 5. Phase diagram for poly(2-vinylpyridine) fractions in toluene, whose weight-average molecular weights are respectively; 1: $50.0\cdot10^4$, 2: $35.9\cdot10^4$, 3: $12.1\cdot10^4$, 4: $3.0\cdot10^4$.

The phase-separation experiments were, therefore, carried out for the P2VP–toluene system and the phase diagrams obtained are depicted in Fig. 5, where the numbers 1 and 2 denote the results for fractions BL21-1 and BL21-3 (in Table 3) and the other numbers, for fractions which were ionically polymerized at the same time (though not given in this Table). The reciprocal of the critical temperature, T_c^{-1}, was plotted in Fig. 6 against $M_w^{-1/2}$, according to the well known equation:[27]

$$1/T_c = (1/\theta)[1+\mathrm{b}/M_w^{1/2}], \tag{7}$$

where b is a constant and θ is the temperature at the theta state. The value of θ determined from the intercept of the line was 63.7 °C.

In Table 3, the M_w evaluated by light scattering in methyl alcohol at 25 °C and the $[\eta]$ in toluene at 63.7 °C for six fractions of P2VP, are summarized. In Fig. 7, $[\eta]$ is plotted against M_w on a double-logarithmic scale, from which the following equation was derived:

$$[\eta]_\theta = 7.54\times10^{-4}\,M_w^{0.5}. \tag{8}$$

The fact that the exponent of M_w is 0.5, indicates

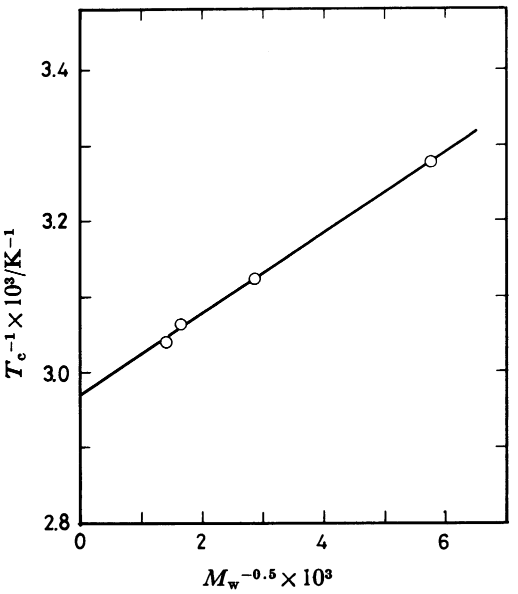

Fig. 6. Plot of reciprocal critical precipitation temperature of poly(2-vinylpyridine) in toluene, $1/T_c$, against $M_w^{-0.5}$.

TABLE 3. LIGHT-SCATTERING AND VISCOSITY DATA IN TOLUENE AT 63.7 °C

Fraction	$M_w\times10^{-4}$	M_w/M_n[a]	$[\eta]_\theta$	$([\eta]_\theta/M_w^{0.5})\times10^4$
C-22	101.4	1.35	0.77	7.65
C-11	62.4	1.23	0.62	7.72
BL21-1	50.0	1.10	0.54	7.63
BL21-3	35.9	1.07	0.44	7.26
C-14	11.8	1.20	0.26	7.48
C-21	3.0	1.15	0.13	7.51
				(average) 7.54

a) Estimated by gel permeation chromatography.

that toluene is a θ-solvent at 63.7 °C for P2VP as predicted from the phase-separation method. Accordingly, the proportionality constant in the above equation was regarded as the K_θ for P2VP at 63.7 °C. The correct value of 7.66×10^{-4} was finally obtained by applying the polydispersity correction of molecular weight in the same manner as before,[12] using the M_w/M_n of each fraction (in Table 3). Here M_n was evaluated by GPC with the DMF solutions. As a result, the value of $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ was estimated to be $-2.4(\pm1.0)\times10^{-3}\ \mathrm{K}^{-1}$ with the K_θ (both in benzene at 16.2 °C and in toluene at 63.7 °C) being expressed as in the following equation:

$$\mathrm{dln}\,\bar{r}^2_0/\mathrm{d}T = (2/3)\mathrm{dln}\,K_\theta/\mathrm{d}T. \qquad (9)$$

This is almost the same as the average value, $-2.3(\pm1.1)\times10^{-3}\ \mathrm{K}^{-1}$, obtained above from the temperature dependence of $[\eta]$ for low-molecular-weight P2VP fractions.

One more additional datum supporting the results obtained in this study was reported earlier by one of us[28]. The distinct negative temperature coefficient of K_θ for P2VP in ethyl alcohol (corresponding to $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T=-2.1\times10^{-3}\ \mathrm{K}^{-1}$, estimated by the Stockmayer-Fixman plot for data of an intrinsic viscosity and molecular weight of ordinary high-molecular-weight P2VP fractions at temperatures from 10° to 65 °C) was noted. It agreed very closely with that of $-2.4\times10^{-3}\ \mathrm{K}^{-1}$ presented here for the same solvent.

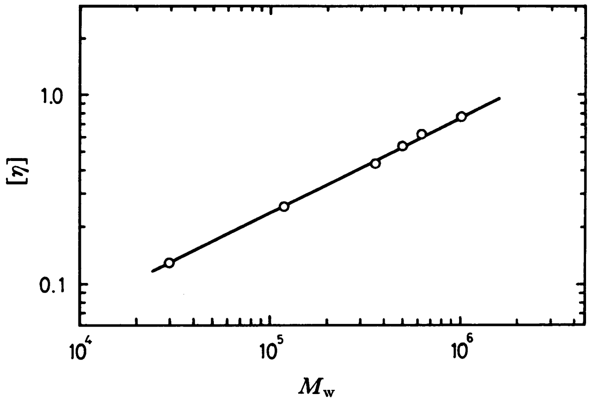

Fig. 7. Double logarithmic plot of $[\eta]_\theta$ against M_w for poly(2-vinylpyridine) in toluene at 63.7 °C.

Thus, we may conclude that the $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ value for P2VP is negative, and its absolute value is considerably larger than those reported for many other polymers; *e.g.*, $-0.17\times10^{-3}\ \mathrm{K}^{-1}$ for polyisobutylene,[9] $-1\times10^{-3}\ \mathrm{K}^{-1}$ for polystyrene[10], $0.48(\pm0.3)\times10^{-3}\ \mathrm{K}^{-1}$ for poly(*p*-chlorostyrene).[4] However, the larger absolute values of $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ have also been reported in the literature; *e.g.*, $-24\times10^{-3}\ \mathrm{K}^{-1}$ for poly(ethylene oxide)[29] and $-4.7(\pm0.91)\times10^{-3}\ \mathrm{K}^{-1}$ for polystyrene.[3] A theoretical investigation of $\mathrm{dln}\bar{r}^2_0/\mathrm{d}T$ for P2VP has not yet been reported, but our results indicate that the extended conformation of P2VP must be associated with lower energies.

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