Solution Properties of Polyvinylpyridine in Acidic Solvent. I. Solution Properties of Poly(2-vinylpyridine) in Aqueous Solution of Sulfuric Acid

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Measurements of the light scattering and viscosity of poly(2-vinylpyridine) (P2VP) in an aqueous (aq) solution of H_2SO_4 at 25 °C were carried out. Although from Stockmayer–Fixman's theory the characteristic ratio (C_∞) was found to be almost constant over the range from 0.1 M to 5.1 M H_2SO_4, the long-range interaction parameter was found to change through the minimum. The difference among the interaction parameters of P2VP and those of poly(4-vinylpyridine) (P4VP) reported before is discussed. Both the second virial coefficient (A_2) and the mean-square radius of gyration ($<s^2>$) of the atactic P2VP sample based on a light-scattering measurement decreased at first with increasing concentration of H_2SO_4, and then increased through the minimum. The variation of A_2 and $<s^2>$ from light scattering with the concentration of H_2SO_4 has the same tendency as that of the intrinsic viscosity ($[\eta]$).

There have been many reports concerning the dilute solution properties of poly(2-vinylpyridine) (P2VP) in organic solvents.1—5) When the nitrogen atom of a residue of P2VP is quaternarized or protonated, this polymer is exhibited as a polyelectrolyte in water. In general, in a solvent of high ionic strength, chain polyelectrolytes have a coiled conformation. As the ionic strength is decreased, the polyelectrolyte coil is expanded due to an electrostatic repulsion between charged segments along the polyion chain or electrostatic excluded volume effect. Recently, there have been several reports concerning the solution properties of quaternarized P2VP.6,7) Light-scattering studies were reported by Schmidt on mostly semi-dilute and concentrated polymer solutions in H_2O.6) In his report, it is shown that anomalous light scattering appears at low concentrations of the polymer (<0.1 mg ml^{-1}), but not at high concentrations. Noda et al. discussed the excluded volume of the quaternarized P2VP using viscosity data measured in aq NaCl solution.7)

It is considered that P2VP is protonated by protons in acidic solvent. However, there have only been a few reports concerning the solution properties of P2VP in acidic solvent.8—10) Loucheux and Rinfret reported on the tacticity dependence of the relationship between the molecular weight and viscosity in 0.1 M HCl and 0.1 M HCl–NaCl solution (1 M=1 mol dm^{-3}).8) Amis et al. reported that the conformation of P2VP in 0.0023 M HCl–ethylene glycol solution can be explained by means of a wormlike chain model.10) Furthermore, the solution properties of poly(4-vinylpyridine) (P4VP), which is a regioisomer to P2VP, in aq H_2SO_4 were reported.11) In that study, it was found that a phase separation appears in some range of the concentration of H_2SO_4. However, in the case of P2VP the phase separation does not appear at any concentration of H_2SO_4, as is demonstrated later. In order to examine the difference between the behaviors of P2VP and P4VP in aq H_2SO_4, the solution properties of P2VP in this solvent were investigated by the method of light scattering and viscosity.

Experimental

Materials. The monomer of P2VP kindly supplied by Tokyo Yukigosei Co. was distilled under reduced pressure immediately before polymerization. In order to obtain P2VP of different tacticity, two polymerization methods were used. Atactic P2VP was polymerized with butyllithium as an initiator in tetrahydrofuran (THF) at −78 °C, and an isotactic polymer with phenylmagnesium bromide in THF at 0 °C.12) Fractionation was carried out by a successive precipitation method using benzene and hexane as a solvent–precipitant pair. The molecular weight of atactic samples (isotacticity: 40—50%) is in the range from $1.0_9\times10^6$ to $3.0_5\times10^4$, and of isotactic samples (isotacticity: 85—90%), from $2.2_6\times10^6$ to $1.5_3\times10^5$.

A light-scattering measurement was carried out with a Fica 50 automatic light-scattering photometer with vertically polarized incident light of 436 nm at 25 °C. Clarification of the solution and solvent was carried out with a Millipore membrane filter "FG" (pore size 0.2 μm). The specific refractive-index increment was measured with a Shimadzu DR-3 type differential refractometer.

The Ubbelohde-type viscometer was used for measuring the viscosity in a water bath controlled within ±0.02 at 25 °C. The pH value at the hightest polymer concentration (<0.1 g dl^{-1}) in 10^{-2} M H_2SO_4 was about 2.2.

The measurement of gel permeation chromatography for P2VP was carried out in *N*,*N*-dimethylformamide with a modified Model 1000/S/401-type apparatus of Water Associate under the following operating condition: μ-styragel columns 10^5, 10^4, 10^3, and 10^6 nm. The polydispersity of P2VP (M_w/M_n) evaluated from the universal calibration curve is in the range from 1.08 to 1.18.

Results and Discussion

Molecular Weight of P2VP in aq H_2SO_4: Since the nitrogen atom of P2VP reacts with H_2SO_4 in aq H_2SO_4 solution, the molecular weight determined from a light-scattering measurement in methanol must be corrected. The extent of H_2SO_4 bound to the monomer unit of P2VP was determined by the same method as that used for P4VP.11) The ratio of molecules of H_2SO_4 to the monomer unit of P2VP was almost unity (0.99—0.96) based on a determination for SO_4^{-2} with barium chloranilate for a sample which was precipitated from the polymer solution by acetone. However, since the concentration of P2VP in 10^{-2} M H_2SO_4 was very low, the protonated polymer was not obtained and the composition of H_2SO_4 for the monomer unit of P2VP in this solvent could not be determined. Assuming that each of the monomer units of P2VP binds with one molecule of H_2SO_4, the molecular weight of P2VP (M) in aq H_2SO_4 was corrected. Afterward, an analysis of the various molecular parameters for P2VP in aq H_2SO_4 was carried out using the corrected value of the molecular weight.

As is well known, a reduced viscosity for the usual chain polyelectrolyte in H_2O increases with decreasing the polymer concentration. However, the viscosity behavior of P2VP in aq H_2SO_4 in this experiment was similar to that of a nonelectrolyte polymer with respect to Huggins and Mead-Fuoss plots. $[\eta]$ could be evaluated by the usual method. The relationships between $[\eta]$ and M in 2.6 and 5.1 M H_2SO_4 are presented in Fig. 1. It is reported that the Mark–Houwink–Sakurada (M–H–S) equation is dependent on the tacticity of P2VP in aq HCl and HCl–NaCl.[8] Recently, it was reported by Yamazaki et al. that the M–H–S equation of polyacrylonitorile in aq nitric acid depends on the tacticity.[13] However, $[\eta]$ of polymers polymerized with phenylmagnesium bromide and butyllithium in this study fell on the same line in a double-logarithmic plot of $[\eta]$ and M. In other words, it is found that the M–H–S equation of P2VP in these solvents is independent of the tacticity. Whether the M–H–S equation depends on the tacticity of the polymer or not may be due to a difference in the content of the stereoregularity for the polymers. The isotactic triad content of P2VP reported by Loucheux and Rinfret might be much higher than that of our samples. However, the difference of the M–H–S equation in these solvents is independent of the isotacticity between 40—50% and 85—90%.

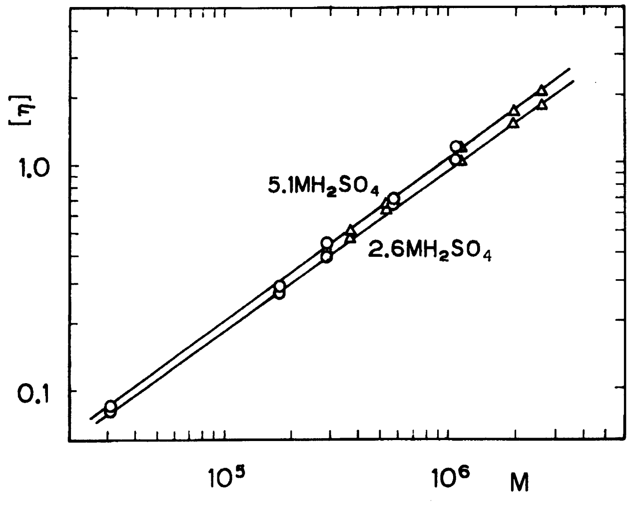

Fig. 1. Double logarithmic plot of $[\eta]$ against M for atactic poly(2-vinylpyridine) (○), isotactic poly(2-vinylpyridine) (△), in 5.1 and 2.6 M H_2SO_4.

The constant K and exponent ν on the M–H–S equations ($[\eta]=KM^{\nu}$) in the measured solvents are listed in Table 1. From Table 1, the value of ν is seen to decrease with increasing H_2SO_4 concentration, and after the minimum, increased. Dzhumadilov et al. reported the same behavior regarding the viscosity for poly(4-vinylpyridine) partially quaternarized with monochloroacetic acid in aq KCl, and assumed that conformation of a macromolecule in solution in the presence of low-molecular-weight ion is controlled by a balance of intramolecular forces.[14] However, in that report, the long-range interaction was not discussed.

The short and long-range interaction parameters of P2VP in this work were evaluated from the data of $[\eta]$ and M in aq H_2SO_4. These two parameters were evaluated with a widely accepted theory: Stockmayer–Fixman equation,[15]

$$[\eta]/M^{1/2} = K_{\Theta} + 0.51\ \Phi_{\mathrm{o}} B M^{1/2}, \tag{1}$$

where

$$K_{\Theta} = \Phi_{\mathrm{o}}(<R^2>_{\mathrm{o}}/M)^{3/2}$$

and

$$B = \beta/m_{\mathrm{s}}.$$

Here, K_{Θ} is related to the unperturbed dimension, $<R^2>_{\mathrm{o}}$, the mean-square unperturbed dimension, Φ_{o} the universal constant, M the molecular weight of the polymer, B the long-range interaction parameter, β the excluded volume, and m_{s} molecular weight of the segment. In Fig. 2, typical examples of Stockmayer–Fixman plots in 10.3, 1, 0.1, and 10^{-2} M H_2SO_4 are shown. K_{Θ} was evaluated based on the intercept of the straight line with the least-squares method. The characteristic ratio (C_{∞}) was evaluated from K_{Θ} using following equation:

$$C_{\infty} = (<R^2>_{\mathrm{o}}/nl^2)_{n=\infty} = (K_{\Theta}/\Phi_{\mathrm{o}})^{2/3}(M_{\mathrm{u}}/2l^2), \tag{2}$$

where n is the number of bonds, l the bond length in the main chain (l=0.154 nm) and M_{u} the monomer molecular weight. The steric factor (σ) is a measure of the flexibility of the polymer chain. In Table 1, the parameters of P2VP in several concentrations of H_2SO_4 are presented together along with the parameters of P4VP calculated with Stockmayer–Fixman equation.[11] The values of C_{∞} or σ are almost constant over the range from 0.1 to 5.1 M H_2SO_4. In other words, the unperturbed dimension of P2VP in these solvents is almost constant. This behavior of P2VP in these solvents is different from that of P4VP.

The value of C_{∞} in 10^{-2} M H_2SO_4 is exceptionally small. Although the protonation degree of a polymer

Table 1. Constants of the Mark–Houwink–Sakurada Equation, Characteristic Ratio (C_∞), Steric Hindrance Parameter (σ), Calculated from Unperturbed Dimension Parameter K_Θ, and Long Range Parameter (B) According to Stockmayer–Fixman's Procedure

[H_2SO_4]	P2VP				P4VP[a)]	
M	10^4K	ν	$C_\infty(\sigma)$	$10^{28}B$	$C_\infty(\sigma)$	$10^{28}B$
0.01	0.81_6	0.87_8	$10._3$ (2.2_7)	8.8		
0.1	3.5_7	0.74_1	$13._8$ (2.6_3)	3.6		
0.25	5.0_7	0.70_2	$13._0$ (2.5_5)	2.2		
0.5	6.2_7	0.68_3	$13._3$ (2.5_8)	1.9		
0.75	5.6_3	0.69_2	$13._2$ (2.5_7)	2.0	$12._0$ (2.4_5)	0.0
1.0	7.4_9	0.67_4	$13._7$ (2.6_2)	2.0	$12._7$ (2.5_3)	0.40
2.6	5.5_6	0.70_4	$13._5$ (2.6_0)	3.1	$14._9$ (2.7_3)	2.0
5.1	4.6_6	0.72_4	$13._9$ (2.6_4)	3.7	$15._8$ (2.8_1)	2.3
10.3	5.1_3	0.72_9	$15._7$ (2.8_0)	3.8	$17._5$ (2.9_6)	2.9

a) Ref. 11.

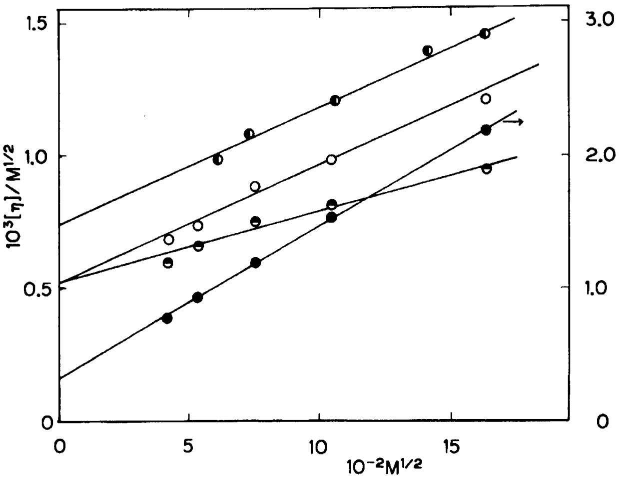

Fig. 2. Stockmayer–Fixman plots for poly(2-vinylpyridine) in aq H_2SO_4; 0.01 M (●), 0.1 M (○), 1 M (◒), and 10.3 M (◐).

in 10^{-2} M H_2SO_4 was not determined, the molecular weight was corrected assuming that the monomer unit of P2VP binds with one molecule of H_2SO_4. It is thought that P2VP at pH 2.2 in aq H_2SO_4 is protonated, since the pK_a value of P2VP is 5.1.[16)] However, according to Kachalosky and Miller, the degree of protonation or ionization for this polymer in aq H_2SO_4 (pH 2.02) is 0.61.[17)] In 10^{-2} M H_2SO_4, the ratio of the monomer unit of P2VP to a molecule of H_2SO_4 may be smaller than one. Consequently, an overestimation of the molecular weight of P2VP in 10^{-2} M H_2SO_4 seems to be the reason for the exceptionally small value of C_∞. The σ value for poly(N-methyl-2-vinylpyridinium chloride) at various NaCl concentrations is 2.8.[7)] The σ values of P2VP (2.55—2.80) are larger than those of polystyrene (2.27)[18)] and P2VP (2.2)[1—4)] in organic solvents. The chain of P2VP in aq H_2SO_4 seems to be more rigid than that in organic solvents.

As can be seen in Table 1, the B value decreased along with an increase of the concentration of H_2SO_4 and increased after taking the minimum, which is in the range from 0.5 to 0.75 M H_2SO_4. It is considered that the variation of $[\eta]$ with the concentration of H_2SO_4 is mainly affected by the term of B. The excluded volume of charged segment β, related to B, can be assumed to consist of an electrostatic part (β_{el}) and a non-electrostatic part (β_o); $\beta=\beta_{el}+\beta_o$. β_o can be obtained by an extrapolation to infinitly large ionic strength. Theoretical treatments of β_{el} have been presented by Manning,[19)] Odijk and Houwaart,[20)] as well as Fixman and Skolnick.[21)] β_{el} is related to the Debye–Hückel screening length. Even if the ionic strength can be related to the concentration of H_2SO_4, β_o or β_{el} could not be evaluated in this study, since β could not be extrapolated to infinitely large ionic strength. In this study, it is difficult to discuss the B or β quantitatively based on the theories. However, the increase of B with increasing concentration of H_2SO_4 may be explained qualitatively. In the case of P4VP[11)] and sulfobetaine polymers,[22)] the same behavior of B was explained in terms of a breakdown of intra- and inter-chain associations. The P2VP chain in aq H_2SO_4, for the sake of a steric hindrance, does not associate so strongly with the P4VP chain, in which a phase separation appears. When the association of the P2VP chain breaks down with increasing H_2SO_4 concentration, the value of B increases. However, when the concentration of H_2SO_4 is very low, the amount of H_2SO_4 which is used to create bridges between the protonated nitrogen atoms is very small. Consequently, the P2VP coil is expanded due to an electrostatic repulsion with decreasing concentration of H_2SO_4, and the value of B increases at low concentrations of H_2SO_4 in the same way as the usual polyelectrolyte in solution with a small amount of an added salt.

The mean-square radius of gyration ($<s^2>$), which is related to the polymer dimension, and the second virial coefficient (A_2), were obtained with light-scattering measurements in order to prove the presence of a minimum of $[\eta]$ for P2VP in aq H_2SO_4. The measured

Table 2. Results of Light-Scattering Measurements and the Intrinsic Viscosity of P2VP (a-10-1) for Several Concentrations of H_2SO_4

$[H_2SO_4]$	$M_{w,app}$	$[\eta]$	$A_{2,app}$	A_2	$<s^2>_z$	γ
M	10^4	10^2 cm^3 g^{-1}	10^{-4} cm^3 g^{-2} mol		10^{-12} cm^2	
0.01	$53._5$	0.50_6	6.0	11	4.7	
0.1	$49._3$	0.40_1	1.3	2.2	3.7	0.14
0.25	$50._7$	0.35_4	1.2	2.1	2.9	0.12
0.5	$50._4$	0.35_2	0.96	1.7	2.7	0.13
0.75	$45._7$	0.34_4	0.84	1.3	2.5	0.09_6
1.0	$45._0$	0.35_7	0.88	1.4	2.8	0.10
5.1	$39._7$	0.44_0	2.2	3.0	3.3	
10.3	$36._2$	0.50_4	2.4	3.0	4.8	

values of the refractive index increment (dn/dc) were in the range from 0.124 in 0.1 M to 0.101 in 10.3 M H_2SO_4 at 25 °C. Since the concentration of the polymer in 10^{-2} M H_2SO_4 is very low, dn/dc in this solvent was determined by extrapolation of the data at several concentrations of H_2SO_4. As can be seen in Fig. 3, a normal Zimm plot of P2VP was obtained for aq H_2SO_4, in contrast to abnormal Zimm plots reported by Schmidt for an alkylated P2VP solution in water at a low concentration of the added salt.[6] The results of light-scattering measurements for a protonated sample, a-10-1 ($M_w=2.88\times10^5$), at several concentrations of H_2SO_4 at 25 °C are listed in Table 2. The molecular weight of the polymer and the second virial coefficient from light-scattering measurements in a multicomponent solvent are apparent values, denoted by $M_{w,app}$ and $A_{2,app}$, respectively. The agreement among the values of $M_{w,app}$ in aq H_2SO_4 was not so good and $M_{w,app}$ were larger than the calculated value (2.88×10^5).

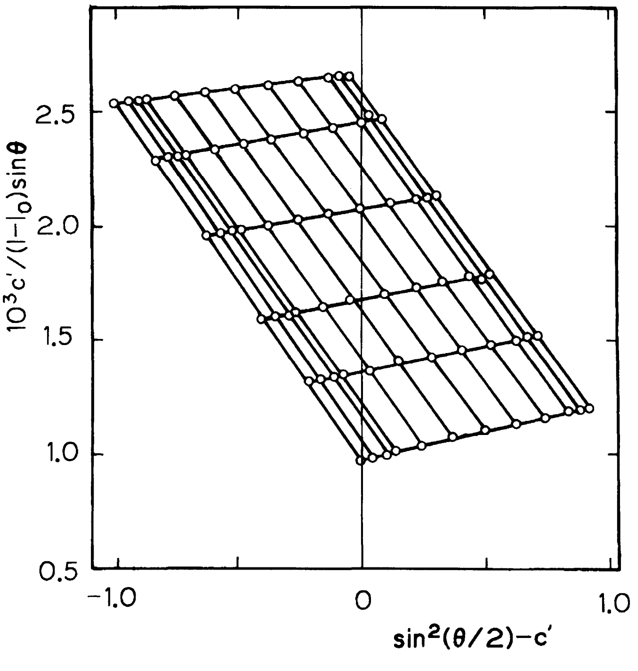

Fig. 3. Zimm plot for atactic P2VP in 10.3 M H_2SO_4 at 25 °C.

The preferential solvation coefficient (γ) proposed by Straziele and Benoit was related to $M_{w,app}$ and M_w,[23]

$$\gamma = [(M_{w,app}/M_w)^{1/2} - 1][(dn/dc)/(dn_o/d\phi)],$$

where $dn_o/d\phi$ is the variation of the refractive index of aq H_2SO_4 with the volume fraction of H_2SO_4. The refractive index of solvent (n_o) was measured with a Shimadzu DR-3 type differential refractometer. However, n_o in 5.1 and 10.3 M H_2SO_4 could not be measured in this apparatus, since n_o is extremly large in these solvents. ϕ was obtained by assuming that the volume of H_2SO_4 can be approximated by the apparent molar volume of H_2SO_4 in aq H_2SO_4. The apparent molar volume of H_2SO_4 was evaluated from the density of aq H_2SO_4 used for the light-scattering measurement. Reasonable values of ϕ were obtained for solutions except for 10^{-2} M H_2SO_4. It was found that the preferential coefficient is in the 0.096—0.14 range. These γ values suggest the possibility of preferential adsorption of H_2SO_4 on P2VP. The coefficients reported for cellulose samples of molecular weight (1.2×10^5 and 5.12×10^4) in aq LiOH are 0.11_7 and 0.088, respectively.[24] The coefficient for zwitterionic polymetylacrylate in 2 M KSCN was reported to be 0.261.[25] Although the γ value in aq H_2SO_4 in this study is comparable to that for cellulose in aq LiOH, it is smaller than that for zwitterionic polymethylacrylate in 2 M KSCN.

The apparent second virial coefficient ($A_{2,app}$) is listed in Table 2 together with the true values (A_2), which were obtained from the following equation:[26]

$$A_2/A_{2,app} = M_{w,app}/M_w. \quad (3)$$

As can be seen in Table 2, the value of A_2 decreased along with an increase in the concentration of H_2SO_4 in the low range from 0.01 to 0.75 M. The variation of A_2 with the concentration of H_2SO_4 is similar to that of an added salt for sodium poly(*p*-styrenesulfate).[27] However, A_2 increased through the minimum with an increase in the concentration of H_2SO_4. The value of $<s^2>$ is not apparent. The variation of $<s^2>$ with the concentration of H_2SO_4 is slightly ambiguous, but similar to that of A_2 and $[\eta]$.

One of authors reported that the values of A_2 and

$[\eta]$ of P2VP ($M=30.08\times10^4$) in methanol at 25 °C are 6.2×10^{-4} $\text{cm}^3\,\text{g}^{-2}$ mol and 1.16 dl g^{-1}, respectively. It seems that P2VP in aq H_2SO_4 has a more compact conformation than that in methanol.[1] The main reason for this difference in the compactness in these solvents is considered to be that of the effect of the long-range interaction. In contrast to P4VP in H_2SO_4, when the concentration of H_2SO_4 is low, the effect of the concentration of H_2SO_4 on $[\eta]$ of P2VP is almost the same as that of an added salt on the usual polyelectrolyte in aq solution. On the other hand, when the concentration of H_2SO_4 is sufficiently high, the behavior of $[\eta]$, that is, the increase of $[\eta]$ with an increase in the concentration of H_2SO_4, is the same as that of P4VP.

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