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Solution Properties of Poly(4-vinylpyridine) in Aqueous Solutions of Sulfuric Acid

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The conformation of poly(4-vinylpyridine) (P4VP) in aqueous solutions of sulfuric acid was studied by light scattering and viscosity measurements at 25 °C. Comparing the experimental intramolecular particle scattering factor ($P(\theta)$) and Debye's theory, it was confirmed that in the Θ-state where the apparent second virial coefficient is zero, the conformation of P4VP is characterized as a Gaussian chain. The intrinsic viscosities of P4VP in aqueous solutions of sulfuric acid of various concentrations were analyzed according to the theoretical equation of Tanaka. The value of the characteristic ratio (C_∞) increased with increasing H_2SO_4 concentration.

Although P4VP is a polyelectrolyte, this polymer is not soluble in water. However, the polyelectrolyte soluble in water was obtained with the quaternarization on the nitrogen of the pyridine residue.[1,2] It was found in a preliminery experiment that the behavior of P4VP in aqueous solutions of H_2SO_4 was different from that in aqueous solutions of HCl and quaternarized P4VP. Namely, solutions of P4VP in aqueous solutions of H_2SO_4 cause a phase separation along with a decrease in the H_2SO_4 concentration. On the other hand, the intrinstic viscosity of P4VP in aqueous solutions of H_2SO_4 increased with an increase in the concentration of H_2SO_4. In addition, it was observed that when Na_2SO_4 was added to a turbid solution the phase separation disappeared. The objectives of this study were to determine the conformation of P4VP in the composition of the Θ-solvent for P4VP with respect to aqueous solutions of H_2SO_4, and to evaluate the value of C_∞ from the relationship between the molecular weight and the intrinsic viscosity for P4VP at several concentrations of H_2SO_4 at 25 °C.

Experimental

Materials: An aqueous solution of 1 M H_2SO_4 (1 M=1 mol dm^{-3}) was purchased from Katayama Chemical and 10.25 M H_2SO_4 from Nacalai Tesque Inc. Aqueous solutions of the measured concentrations of H_2SO_4 used in this study were obtained by dilution of these two master solutions.

The monomer of 4-vinylpyridine was distilled under reduced pressure immediately before use. Polymerization was carried out with butyllithium used as an initiator in tetrahydrofuran at −78 °C. In order to obtain a larger molecular-weight sample, radical polymerization was carried out with azobisisobutyronitrile as an initiator at 50 °C. The fractionation was carried out by a successive precipitation method using 2-methyl-2-propanol and benzene as a solvent–precipitant pair.

The Ubbelohde-type viscometer was used to measure the viscosity in a water bath controlled within ±0.02 °C at 25 °C.

A light-scattering measurement was carried out with a Fica 50 automatic light-scattering photometer with vertically polarized incident light of 436 nm at 11 different angles ranging from 30° to 150°. An optical clarification of each solution and solvent was carried out through a Millipore membrane filter "FG" (pore size 0.2 μm). Antifluorescence filter (436 nm) was also used to protect the fluorescence effect, which was not confirmed to be significant. The specific refractive-index increment was measured with a Shimadzu DR-3 type refractometer.

The absorption spectrum at 530 nm was measured with a UVIDEC-670 spectrophotometer of Japan Spectroscopic Co., Ltd.

Results and Discussion

Since the phase separation of a P4VP solution was found to occur along with a decrease in the H_2SO_4 concentration at 25 °C, the Θ-solvent should be determined by some suitable method. In this study light-scattering method was used to determine the Θ-solvent composition. The analysis of light scattering data for P4VP in aqueous solutions of H_2SO_4 can be treated in the same way as that for a nonelectrolyte polymer–solvent system if the sample solution is dialyzed before making a measurement.[3] However, if this is not the case, the molecular weight and second virial coefficient obtained from usual light-scattering method are apparent values: $M_{\mathrm{w,app}}$ and $A_{2,\mathrm{app}}$. Nevertheless, when A_2 is zero, $A_{2,\mathrm{app}}$, should also be zero; Θ-solvent can thus be determined by light scattering without carrying out dialysis. In Fig. 1, a typical Zimm plot of sample A-1 ($M_\mathrm{w}=432\times10^4$) in 0.85 M H_2SO_4 at 25 °C is presented. Obviously, $A_{2,\mathrm{app}}$ is equal to zero. The observed values of $A_{2,\mathrm{app}}$ for A-1, B-1 ($M_\mathrm{w}=26.5\times10^4$), add C-1 ($M_\mathrm{w}=6.0\times10^4$) are plotted against the concentration of H_2SO_4 at 25 °C in Fig. 2. It was found that the points at which $A_{2,\mathrm{app}}$ is equal to zero are scattered for the measured samples. The concentration of H_2SO_4 at which $A_{2,\mathrm{app}}$ is equal to zero for sample A-1 was determined to be 0.85 M; this is assumed to be with the Θ-solvent at 25 °C. On the other hand, the concentration of H_2SO_4 at $A_{2,\mathrm{app}}=0$ for samples B-1 and C-1 was assumed to be 0.75 M H_2SO_4 according to an accidental experimental error. However, since sample A-1 was turbid in this composition, no light-scattering measure-

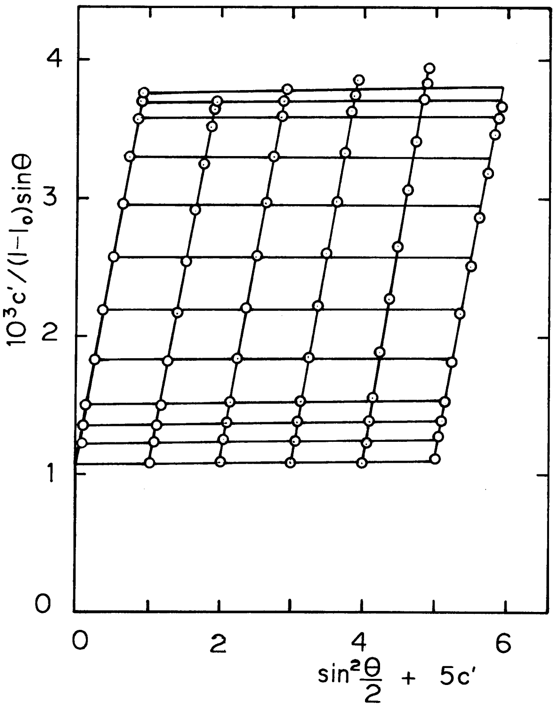

Fig. 1. Zimm plot for P4VP (sample A-1; M_w=432× 10^4) in 0.85 M H_2SO_4 at 25 °C.

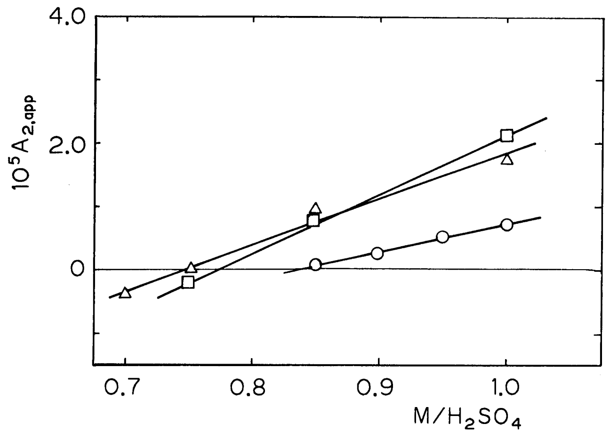

Fig. 2. Dependence of the apparent second virial coefficient, $A_{2,app}$, on the concentration of H_2SO_4 at 25 °C. ○, A-1; △, B-1; □, C-1.

ment was carried out. The concentration of H_2SO_4 at which $A_{2,app}$ is zero may be dependent on the molecular weight of this polymer.

It has been shown that the intramolecular particle scattering factor ($P(\theta)$), and the mean-square radius of gyration ($<s^2>$) obtained from light-scattering data without carrying out dialysis are not apparent, but, rather, true values. There is thus the following relation between the Rayleigh ratio (R_θ) and $P(\theta)$ at a scattered angle of θ:

$$(K'c/R_\theta)_{c=0}=(K'c/R_\theta)_{c=0,\theta=0}/P(\theta)=1/\{M_{w,app}\times P(\theta)\}.$$

Here K' is the apparent optical constant, expressed as

$$K'=2\pi^2n_0{}^2(dn/dc)^2/N_A\lambda_0{}^4,$$

where n_0 is the refractive index of the solvent, λ_0 the wavelength of the light in a vacuum and (dn/dc) the refractive index increment. The value of $P(\theta)$ at any θ can thus be evaluated from Zimm plots. Namely, the reciprocal $P(\theta)$ can be expressed in terms of $\sin^2(\theta/2)$ as follows:

$$P^{-1}(\theta)=1+(16\pi^2/3\lambda^2)<s^2>\sin^2(\theta/2)+\cdots, \qquad (1)$$

where λ is the wavelength in the solvent. In Θ-solvent, $P(\theta)$ for a Gaussian chain was given by Debye[4] as

$$P(\theta)=2u^{-2}[\exp(-u)-1+u], \qquad (2)$$

where $u=(16\pi^2/\lambda^2)<s^2>_0\sin^2(\theta/2)$ and $<s^2>_0$ is the unperturbed mean-square radius of gyration of the polymer.

$P(\theta)$ for a rod-like polymer is as follows:[5]

$$P(\theta)=(1/x)\int_0^{2x}\{(\sin u)/u\}du-\{(\sin x)/x\}^2, \qquad (3)$$

where $u=2\pi L\sin(\theta/2)/\lambda$ and L is the rod length.

In an analysis of the data for light scattering with a Fica 50 instrument, the following relations were used:

$$\{K''c'/R(\theta)\}_{c=0,\theta=0}=1/M_{w,app}$$

and

$$\{K''c'/R(\theta)\}_{c=0}=1/(M_{w,app}\times P(\theta)\}.$$

Here, K'' is are constant. The $P(\theta)$ from the ratio of the intercept values at c=0 and θ=0 to the value of the intercept at c=0 can be evaluated. Other methods used to evaluate the $P(\theta)$ related to $<s^2>$ have been proposed by Berry[6] and Fujita.[7] In our study, the usual method was to calculate the $P(\theta)$ from Zimm plots by a least-squares method with respect to the relation between c' and $K''c'/R(\theta)$ at the respective scattered angle (θ). The value of $<s^2>_0$ was calculated using Eq. (1). Berry's method[6] was to use

$$P^{-1/2}(\theta)=1+(8\pi^2/3\lambda^2)<s^2>\sin(\theta/2)+\cdots \qquad (4)$$

and Fujira's method[7] was to use

$$P^{-1/2}(\theta)=1+(32\pi^2/3\lambda^2)<s^2>Z(v), \qquad (5)$$

where $Z(v)=P^{-1}(\theta)v^{-4/3}\int_0^v P(\theta)v\,dv$ and $v=\sin^3(\theta/2)$. The values of $<s^2>^{1/2}$ for sample A-1 obtained from the above equations were 70 nm from usual method, 66 nm from Berry's method and 63 nm from Fujita's method. The values for sample B-1 from usual, Berry's and Fujita's methods were evaluated to be 38, 36, and 34 nm, respectively. However, since the molecular weight of C-

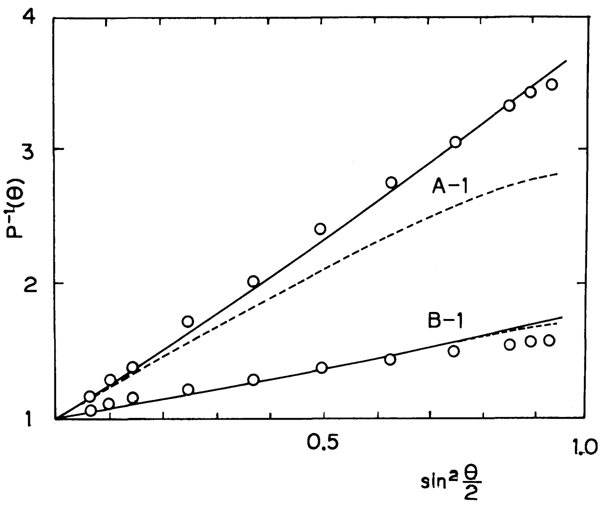

Fig. 3. Comparison of the measured P^{-1} (θ) (○) with the theoretical values calculated from Eq. 2 (solid line) and Eq. 3 (dotted line) using 66 nm for A-1 and 36 nm for B-1.

1 is very low, the value of $P(\theta)$ for this sample obtained from the light-scattering measurement is very small. No believable value of $<s^2>^{1/2}$ for C-1 could be evaluated. The measured values of $P^{-1}(\theta)$ for these samples in 0.85 and 0.75 M H_2SO_4 and the calculated theoretical lines of Debye (Eq. 2), in which $<s^2>^{1/2}=66$ nm for A-1 and 36 nm for B-1, are given together along with the theoretical values of $P(\theta)$ for rod-like chain (Eq. 3) by the dotted line in Fig. 3. As can be seen in Fig. 3, the theoretical line with the rod-like chain for A-1 was deviated from the measured values. Good agreement between the measured values of $P^{-1}(\theta)$ and those calculated from Eq. (2) regarding A-1 was found. However, very good agreement with theory regarding the rod-like chain and Gaussian distribution of segments was obtained for $P(\theta)$ in the case that $<s^2>^{1/2}=36$ nm, except for the large value of $\sin^2(\theta/2)$. Consequently, no information concerning the conformation of P4VP in aqueous solution of H_2SO_4 was obtained from the $P(\theta)$ values of B-1. Generally, when the molecular weight of the polymer was changed, the conformation of polymer in the same solvent and at the same temperature did not change. It may therefore, be assumed that in 0.75 M H_2SO_4, the coils of P4VP at 25 °C have a Gaussian distribution of segments.

Table 1. The Constants in 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 the Tanaka's Procedure

Concn of H_2SO_4/M	10^4K	ν	$C_\infty(\sigma)$	$10^{28}B$
0.75	4.2_6	0.50_2	$12._1(2.4_5)$	0
0.85	3.1_6	0.53_6	$12._7(2.5_2)$	0.4
1.0	1.8_6	0.58_6	$13._0(2.5_5)$	1.2
(20.5/8)	0.96_8	0.66_2	$14._2(2.6_7)$	3.7
(20.5/4)	0.91_6	0.67_4	$14._9(2.7_3)$	4.6
(20.5/2)	0.87_6	0.69_0	$16._7(2.8_9)$	7.5

Relation between the Molecular Weight (M_w) and the Intrinsic Viscosity ([η]). After P4VP dissolved in H_2SO_4 was poured into acetone, the salt of P4VP and H_2SO_4 was obtained. After drying the salt with P_2O_5 in a desiccator, the content of H_2SO_4 in the salt was determined with barium chloranilate at 530 nm. By analyzing the polymer salt, it is found that the ratio of H_2SO_4 molecule to the monomer unit of P4VP was almost one (0.97—0.93). From this result, the molecular weight of the polymer in H_2SO_4 was evaluated from the molecular weight of P4VP by assuming that one molecule of H_2SO_4 reacts with a monomer unit of P4VP.

The constant K and the exponent ν of the Mark–Houwink–Sakurada equation (M–H–S equation) at 25 °C at various concentrations of H_2SO_4 are given in Table 1. It was found that the ν is $0.5 \leqq \nu < 0.8$ from theory[8,9] when the polymer chain in a solution takes a random coil (Gaussian distribution of segments) form. The ν in these solvents ranged between 0.5 and 0.7. It is believed that the conformation of P4VP in this study is a random coil. The conclusion from the M–H–S equation was in good agreement with that from $P(\theta)$. It was found that in an aqueous solution of 0.75 M H_2SO_4, ν of M–H–S equation is 0.50_2, and that it increases with increasing H_2SO_4 concentration.

Estimation of the Unperturbed Dimension. According to the theory of Flory and Fox,[10] the constant K_θ is related to the unperturbed mean-square end-to-end distance ($<R^2>_0$) according to

$$K_\theta = \Phi_0(<R^2>_0/M)^{3/2},$$

where Φ_0 is the universal constant and M the molecular weight of the polymer. When we measure the dilute solution properties of a polymer in a non-Θ-solvent, the value of K_θ must be indirectly estimated by an extrapolation method based on two-parameter theory. In this study, the unperturbed dimension was evaluated using an equation derived from widely accepted theory, the Tanaka equation[11]

$$([\eta]/M^{1/2})^{5/3} = K_\theta^{5/3} + 0.627\Phi_0 K_\theta^{2/3} B M^{1/2}. \qquad (6)$$

The results of an analysis of Tanaka's equation are given in Fig. 4; K_θ was evaluated from the intercept of a straight line using the least-squares method.

The characteristic ratio (C_∞) for P4VP salt at six concentrations of H_2SO_4 was calculated using the following equation and the K_θ values evaluated as described above:

$$C_\infty = (<R^2>_0/nl^2)_{n=\infty} = (K_\theta/\Phi_0)^{2/3}\{M_u/(2l^2)\}.$$

Here, n is the bond number, l the bond length in the main

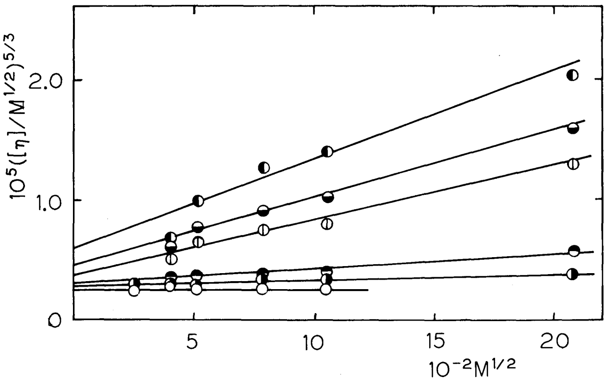

Fig. 4. Tanaka plots of P4VP. Solvent: ◐, (20.5/2) M; ◒, (20.5/4) M; (⦶), (20.5/8) M; ◓, 1 M; ◑, 0.85 M; ○, 0.75 M H_2SO_4 at 25 °C.

chain (l=0.154 nm for C–C bond) of the vinyl polymer and M_u the monomer molar mass. The values of C_∞ evaluated using the above equations are summarized in Table 1, along with the steric factor (σ), which is the ratio of $<R^2>_0^{1/2}$ to $<R^2>^{1/2}_{0f}$ of the hypothetical chain with completely free rotation around the C–C backbone bond, as a measure of the flexibility of the linear polymer chain. It was found that the value of C_∞ increased with increasing the H_2SO_4 concentration.

Regarding the value of σ for P4VP, 2.37 has been reported in ethanol.[12] In 0.75 M H_2SO_4 where $A_{2,\mathrm{app}}$ is almost zero, σ=2.45 indicates a slight rigidity. It has been reported that the value of σ for fully charged poly(acrylic acid) (2.38) is slightly larger than that of the acid form (1.85).[13] On the other hand, for P2VP, which has a similar conformation as that for P4VP, the value of σ in organic solvents is 2.28.[14] The value of σ for poly(N-methyl-2-pyridinium chloride) in aqueous solutions of NaCl is 2.8.[15] For poly[(2-vinylpyridinio-1-propanesulfonate], whose $[\eta]$ increases with the addition of a salt, σ is 2.65 (C_∞=14.0) in 0.01 M NaCl.[16] This value (C_∞=14.0) is comparable to that of P4VP in (20.5/8)M H_2SO_4.

Although a solution of P4VP in 0.1 M H_2SO_4 becomes turbid and phase separation occurs at 25 °C, P4VP can be dissolved in a mixed solvent (0.1 M H_2SO_4 and 1 M Na_2SO_4). The M–H–S equation for this mixed solvent is $[\eta]=1.5_9\times10^{-4}\,M_w^{0.604}$. A detailed discussion on the solution properties of P4VP in this mixed solvent will be reported later.

A qualitative explanation of the solution properties of P4VP in H_2SO_4 is as follows: It seems that although the proton (H^+) from H_2SO_4 protonates the nitrogen atom of the pyridine ring of the polymer, they do not effect on the intrinsic viscosity when the concentration of H^+ is 0.1 M. This has been confirmed by the fact that $[\eta]$ of P4VP in 0.1 M HCl showed the same behavior as did the nonelectrolyte linear polymer in the usual solvent. Furthermore, the turbidity of P4VP in 0.1 M H_2SO_4 disappeared upon the addition of Na_2SO_4 or SO_4^{2-}. Thus, SO_4^{2-} seems not only to mask the charge on the protonated nitrogen atom of the pyridine ring, but also to create a bridge between the protonated nitrogens. Phase separation occurs due to the formation of SO_4^{2-} bridges. As the concentration of SO_4^{2-} increases, the bridges eventually break down and the solution becomes clean. Any further addition of H_2SO_4 may promote solubility and chain expansion. Consequently, $[\eta]$ of P4VP increases with increasing H_2SO_4 concentration. Further, the C_∞ or σ of P2VP, which is a similar polymer to P4VP, depends on the nature of the solvent.[14] It is thought that the solution properties of P4VP in aqueous solutions of H_2SO_4 are the same as those of P2VP in organic solvents.

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