The Specific Refractive Index Increment and the Partial Specific Volume of Atactic Poly(2-vinylpyridine)

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The specific refractive index increment, dn/dc, of atactic poly(2-vinylpyridine) was measured in 18 solvents with 436 nm light at 25 °C. Using these data, the partial specific volume, $\bar{v}_2$, of the polymer in these solvents was then evaluated by means of the method proposed by Heller. A sufficient agreement was found between the values of $\bar{v}_2$ thus obtained optically and those determined directly by the density measurement of solutions in several solvents. It was found that $\bar{v}_2$ varies considerably with the kind of solvent and that, in some solvents, such as methanol and ethanol, it takes an extremely lower value than that of bulk crystalline isotactic poly(2-vinylpyridine). The results were discussed in terms of thermodynamic interactions between the polymer and the solvent, the molar volume, and the compressibility of the solvent molecule. The relationship between dn/dc and the refractive index of a solvent, n_1, for 436 nm light is expressed by dn/dc=0.900 × (1.628−n_1).

The specific refractive index increment, dn/dc, of a dilute solution of a polymer is indispensable for an investigation of the polymer in solution by light scattering. Besides, the partial specific volume of a polymer, $\bar{v}_2$, is not only a very important value, often appearing in various parameters representing thermodynamic and hydrodynamic interactions between polymer and solvent, for example, the second virial coefficient, A_2, but also $\bar{v}_2$ itself is a useful quantity, showing polymer-solvent interactions. On the other hand, the very intimate relationships between the dn/dc and the $\bar{v}_2$ of a polymer in solution have been intensively studied by many investigators.

In spite of the ever-increasing number of related papers[1–3] on the solution properties of poly(2-vinylpyridine), there has been no systematic investigation of the dn/dc and the $\bar{v}_2$ of this polymer. Because of the very strong interactions between this polymer and certain solvents,[3–5] some specific characteristics can be expected to exist in the $\bar{v}_2$ of this polymer in those solvents which may be absent in a non-polar polymer such as polystyrene dissolved in a non-polar solvent.

The objects of this work are, first, to perform the direct measurement of the dn/dc of atactic poly(2-vinylpyridine) in as many solvents as possible; the results will enable us to make a broader choice of the solvent in light-scattering measurements of this polymer, and second, to evaluate the value of $\bar{v}_2$ according to the method proposed by Heller,[6] using the dn/dc data. The values of $\bar{v}_2$ thus obtained will be compared with those measured densitometrically in several solvents, and the relationship between the $\bar{v}_2$ and various properties of the solvents will be discussed.

Experimental

Specific Refractive Index Increment. The specific refractive index increments were measured photometrically with a Shimadzu DR-3-type differential refractometer.[7] All the measurements were carried out using the blue light of Hg (436 nm). The temperature in the cell was controlled at 25±0.01 °C. The instrumental constant was carefully calibrated with the standard aqueous solutions of KCl[8] and sucrose;[9] it was agreed within the range of 1.5%. The specific refractive index increment of the standard polystyrene, obtained from the Pressure Chemicals Co., in benzene at 25 °C for the 436 nm light gave experimental values ranging from 0.109 to 0.111, within the range of values reported in the most recent literature.[7]

Refractive Index of the Solvent. The refractive index of the solvent was measured with a Pulfrich refractometer manufactured by the Shimadzu Co. with 436 nm light of Hg at 25±0.05 °C. The calibration of the instrument was done as usual.[10]

Refractive Index of Bulk Atactic Poly(2-vinylpyridine). The refractive index of bulk atactic poly(2-vinylpyridine) was measured with an Abbe-type refractometer manufactured by the Atago Kogakukikai Co. at 25±0.05 °C with 436 nm light of Hg. A thin film of the atactic poly(2-vinylpyridine) made from a benzene solution on mercury was placed on the major prism demounted from the instrument and carefully warmed to 115 °C in a nitrogen atmosphere. That temperature was then maintained for 15 hr. As the glass-transition temperature of this polymer is 104 °C,[11] a close adherence of the film to the surface of the prism was attained, and the border line between light and shade could be recognized. After the measurements had been completed and the film on the prism had been removed by dissolving with methanol, the calibration of the instrument was done as usual.[10]

Density of Solution. Measurements of the density of the polymer solution in several solvents were made with a usual Ostwald-Sprengel-type pycnometer. For solutions in benzene and dioxane, the density was measured by means of a graduated pycnometer. The concentrations of the polymer ranged from 1×10^{-2} to 6×10^{-2} in the weight fraction of the polymer. The temperature of the bath was maintained at 25±0.002 °C.

Density of Bulk Atactic Poly(2-vinylpyridine). The density of bulk atactic poly(2-vinylpyridine) was measured with the Weld-type pycnometer, immersing the thin film in decahydronaphthalene at 20±0.002 °C. The temperature coefficient of the volume expansion of the polymer was measured with a dilatometer manufactured by Shibayama Kagakukikai Co.; thus the value of the density of the polymer at 25 °C was determined. The density of the bulk isotactic crystalline poly(2-vinylpyridine) was measured in the same way, but directly at 25 °C.

Viscosity. The limiting viscosity number, [η], of poly(2-vinylpyridine) in a number of solvents was determined in a Ubbelohde-type viscometer at 25±0.01 °C. The values of [η] were obtained by plotting η_{sp}/c against the concentration, c, and by extrapolating to a zero concentration.

Polymers. The polymerizations and fractionations of atactic and isotactic poly(2-vinylpyridine) were all the same as those previously reported.[12,13] The crystallization of a fraction of isotactic poly(2-vinylpyridine) was performed by heating it at 150 °C for a night in a nitrogen atmosphere; its crystallinity was checked by the X-ray diffraction method.[13,14]

Solvents. All the solvents used in this experiment were of a reagent grade; some of them had been dried and fractionally distilled.

Results and Discussion

Recent advances in both the theory and practice of the influence of a solvent on the specific refractive index increment, d*n*/d*c*, including the proposals of Heller,[6] Bodmann,[15] and Mächtle and Fischer,[16] have been summarized in the monograph by Huglin.[7] These theories are based on the concept of the specific refraction, *R*, which is a constant value and is a function of the specific volume, *v*, and the refractive index, *n*, of the component. The expressions for *R* proposed by Gladstone-Dale, Lorenz-Lorentz, and Eykman are:[7]

$$\text{Gladstone-Dale (GD)}: R = (n-1)v \tag{1}$$

$$\text{Lorenz-Lorentz (LL)}: R = [(n^2-1)/(n^2+2)]v \tag{2}$$

$$\text{Eykman (Ey)}: R = [(n^2-1)/(n+0.4)]v \tag{3}$$

According to the theory of the mixing rule,[17] the specific refraction of a binary solution can be expressed by:

$$R_{12} = R_1 w_1 + R_2 w_2 \tag{4}$$

where R_i and w_i are the specific refraction and the weight fraction of the component, *i*, respectively, and where $i=1$, 2, and 12 refer to the solvent, the solute, and the solution respectively. Equation (4) is correct only when there is no volume change upon mixing in the component, when the polarizability of the components is the same before and after mixing and when the solute is spherically symmetrical isotropic.[6]

For the polymer-solvent system where the volume change of mixing cannot be neglected, Heller[6] derived an expression of the relationship between d*n*/d*c* and the partial specific volume of a polymer, $\bar{v}_2$, in solution at an infinite dilution, assuming Lorenz-Lorentz expression, Eq. (2), for the specific refraction of each component. The final expression of Heller is:

$$[\mathrm{d}n/\mathrm{d}c]_{c=0} = 3\bar{v}_2(B-A)/2n_1(1-A)^2 \tag{5}$$

$$A = (n_1{}^2-1)/(n_1{}^2+2)$$

$$B = (n_2{}^{*2}-2)/(n_2{}^{*2}+2)$$

where n_1 is the same as above and where $n_2{}^*$ is the refractive index of the polymer in solution. Heller assumed further that the Lorenz-Lorentz relation for a single component system:

$$(\varepsilon-1)/(\varepsilon+2) = 4\pi N\alpha/3 \tag{6}$$

where ε is the optical dielectric constant; α, the polarizability, and *N*, the number of molecules in a unit of volume, is valid for not only a bulk polymer but also for polymer in a very dilute solution if the polarizability of the polymer does not change measurably before and after mixing, even if the volume change can not be neglected. Then the following relationship must hold:

$$R_{2,\mathrm{He}} = (n_2{}^2-1)/(n_2{}^2+2)\rho_2$$

$$= [(n_2{}^{*2}-1)/(n_2{}^{*2}+2)]\bar{v}_{2,\mathrm{op}} = \text{constant} = k \tag{7}$$

where ρ_2 is the density of the bulk polymer.

If we can obtain the values of n_2 and ρ_2 of the bulk polymer, the value of *k* in Eq. (7) can be determined. Then, using Eqs. (5) and (7), a series of tentative pairs of $\bar{v}_{2,\mathrm{op}}$ and d*n*/d*c* can be obtained. Thus, the true value of $\bar{v}_{2,\mathrm{op}}$ can be evaluated graphically using the experimental value of d*n*/d*c*.

Another analytical method for obtaining $\bar{v}_{2,\mathrm{op}}$ was reported by Heller[18] in his second series concerned with the optical determination of the partial specific volume of macromolecules in solution. From Eq. (5) we can obtain:

$$\bar{v}_{2,\mathrm{op}} = k/A - f(\mathrm{d}n/\mathrm{d}c) = R_{2,\mathrm{He}}/A - f(\mathrm{d}n/\mathrm{d}c) \tag{8}$$

$$f = (2/3)n_1(1-A)^2/A \tag{9}$$

From Eq. (8), $\bar{v}_{2,\mathrm{op}}$ can then be readily calculated by using our knowledge of $R_{2,\mathrm{He}}$, d*n*/d*c*, and n_1 and/or *A*.

The usefulness of Heller's method for the evaluation of $\bar{v}_2$ from the d*n*/d*c* data has been confirmed recently;[19] also, Scholte[20] obtained an equation identical with Eq. (5) on the same assumption as Heller's but with a rather different approach.

Another approach made by Bodmann[15] concerning the relationship between d*n*/d*c* and the $\bar{v}_2$ of the polymer at an infinite dilution established that the R_{12} should be expressed by the partial specific refractions, $\bar{R}_1$ and $\bar{R}_2$, instead of R_1 and R_2 in Eq. (4); Bodmann's final expressions for $\bar{R}_2$ for the three functions, Eqs. (1), (2), and (3) were as follows:

$$\bar{R}_{2,\mathrm{GD}} = [(n_1-1)\bar{v}_2] + (\mathrm{d}n/\mathrm{d}c) \tag{10}$$

$$\bar{R}_{2,\mathrm{LL}} = [(n_1{}^2-1)/(n_1{}^2+2)]\bar{v}_2 + [6n_1/(n_1{}^2+2)](\mathrm{d}n/\mathrm{d}c) \tag{11}$$

$$\bar{R}_{2,\mathrm{Ey}} = [(n_1{}^2-1)/(n_1+0.4)]\bar{v}_2 + [(n_1+0.84)/(n_1+0.4)^2](\mathrm{d}n/\mathrm{d}c) \tag{12}$$

Equations (5) and (11) are equivalent when the specific refraction, $R_{2,\mathrm{He}}$ (Eq. (7)), is equal to the partial specific refraction, $\bar{R}_{2,\mathrm{LL}}$ (Eq. (11)), because only under this condition can Eq. (5) be derived from Eq. (11).

Examinations were made into the $\bar{R}_2$ values for the three functions calculated from the data of the densitometrically determined values of n_1, d*n*/d*c*, and $\bar{v}_{2,\mathrm{d}}$ in seven solvents; the results will be discussed later.

The results of the measurement of the refractive index of a pure solvent at 25 °C with 436 nm light, all of which were used for the d*n*/d*c* measurements, are shown in the third column of Table 1.

The refractive index increment for a fraction of atactic poly(2-vinylpyridine) ($M_\mathrm{w}=5.5\times10^4$) in several solvents is plotted against the concentration in Fig. 1. The linearity is satisfactory in all the solvents measured. The resultant values of d*n*/d*c* in all the solvents obtained by the least-squares method are shown in the fourth column of Table 1.

The value of the refractive index of a fraction of atactic poly(2-vinylpyridine) ($M_\mathrm{w}=34.7\times10^4$) in bulk for 436 nm light at 25 °C was 1.622. The specific volumes of three fractions of the same polymer ($M_\mathrm{w}=44.7\times10^4$, 34.7×10^4, and 19.0×10^4) at 20 °C were, on the average, 0.895, 0.896, and 0.895 cm^3/g respectively.

TABLE 1. PARTIAL SPECIFIC VOLUME $\bar{v}_{2,\mathrm{op}}$ OF ATACTIC POLY(2-VINYLPYRIDINE) OBTAINED OPTICALLY

No.	Solvent	n_1	dn/dc	$\bar{v}_{2,\mathrm{op}}$ a)	Δ b)	δ c)	$[\eta]$	$(0.5-\chi_1)/V_1\times10^4$	V_1	κ_s d)
1	1,1,2,2-Tetrachloroethane	1.5040	0.109	0.884	1.4	4.4	1.06	3.96	105.7	45.8
2	Aniline	1.6168	0.023	0.874	2.6	3.2	1.05	3.93	91.5	35.6
3	2-Butanol	1.4022	0.216	0.845	5.8	−0.2	0.99	3.66	92.9	81
4	Chloroform	1.4536	0.168	0.848	5.5	0.1	0.99	3.58	80.7	67.1
5	n-Propanol	1.3912	0.215	0.842	6.1	−0.6	0.96	3.30	75.1	82.8
6	Methanol	1.3334	0.270	0.798	11.0	−5.8	0.90	3.06	40.7	100.1
7	n-Butanol	1.4021	0.209	0.838	6.6	−1.1	0.87	2.61	92.0	76.9
8	Ethanol	1.3671	0.245	0.809	9.8	−4.5	0.81	2.26	58.7	92.5
9	1,2-Dichloroethane	1.4539	0.148	0.885	1.3	4.5	0.73	1.66	79.4	55
10	Cyclohexanone	1.4591	0.144	0.885	1.3	4.5	0.71	1.50	97.2	50.2
11	Dimethylformamide	1.4411	0.165	0.872	2.8	3.0	0.58	0.74	77.4	
12	2-Propanol	1.3832	0.221	0.841	6.2	−0.7	0.54	0.57	75.1	93.2
13	1,1,1-Trichloroethane	1.4484	0.162	0.866	3.5	2.2	0.52	0.38	100.4	
14	Tetrahydrofuran	1.4135	0.195	0.851	5.1	0.5	0.51	0.37	81.7	
15	Nitroethane	1.4043	0.197	0.860	4.1	1.5	0.48	0.20	71.9	
16	Benzene	1.5192	0.107	0.868	3.2	2.5	0.48	0.19	89.5	64.9
17	Dioxane	1.4296	0.175	0.869	3.1	2.6	0.42	−0.02	85.7	50.1
18	Methylethylketone	1.3869	0.215	0.849	5.4	0.2	0.31	−0.37	91.5	83.8

a) $\bar{v}_{2,\mathrm{op}}$=the values obtained with Eq. (5) in combination with Eq. (7). b) Δ=per cent deviation of $\bar{v}_{2,\mathrm{op}}$ relative to the specific volume of bulk atactic poly(2-vinylpyridine) $v_{2,\mathrm{a}}$. c) δ=per cent deviation of $\bar{v}_{2,\mathrm{op}}$ relative to the specific volume of bulk isotactic crystalline poly(2-vinylpyridine) $v_{2,\mathrm{c}}$. d) κ_s=adiabatic compressibility of solvent at 25 °C and 1 atmosphere. Ref.: "Chemical Hand Books, Part II", ed. by Chem. Soc. Japan, Maruzen, Tokyo (1966), p. 485

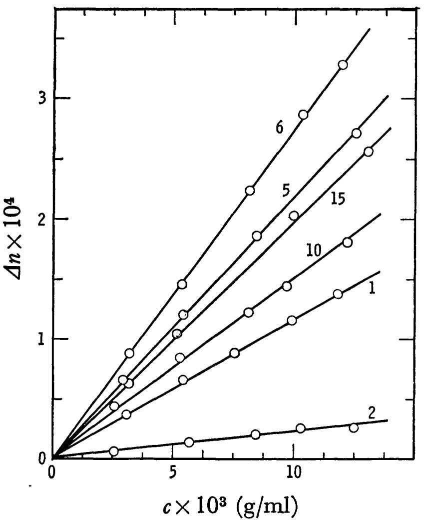

Fig. 1. Plots of the refractive index increment Δn vs. concentration c for atactic poly(2-vinylpyridine) at 25 °C. λ=436 nm. The numbers on the lines correspond to those in Table 1.

The mean value of these three values is 0.895 cm^3/g. The volume-expansion coefficient of this polymer, as determined by dilatometry, was 3.0×10^{-4} cm^3/g °C, so that the specific volume of this polymer at 25 °C was 0.897 cm^3/g.

In Fig. 2 the values of the partial specific volume, $\bar{v}_{2,\mathrm{d}}$ of the polymer at 25 °C, obtained by densitometric measurements of the solution in seven solvents, are plotted against the weight fraction of the polymer. The $\bar{v}_{2,\mathrm{d}}$ value at each concentration was calculated, using the data of the density of a solution, with Kraemer's equation:[21,22)]

$$\bar{v}_{2,\mathrm{d}} = 1/\rho_{12}\{1-[(1-w_2)/\rho_{12}](\mathrm{d}\rho_{12}/\mathrm{d}w_2)\}$$

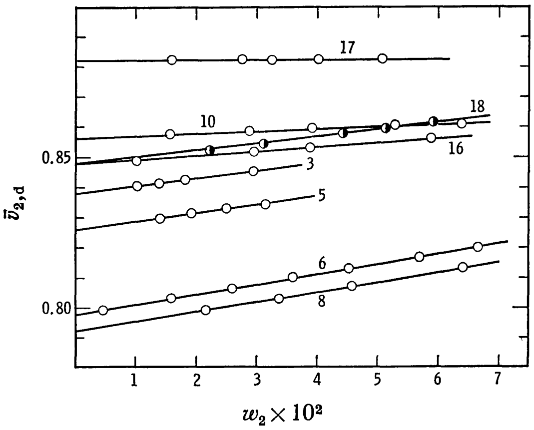

Fig. 2. Plots of the partial specific volume $\bar{v}_{2,\mathrm{d}}$ of atactic poly(2-vinylpyridine) evaluated by densitometrically vs. concentration w in weight fraction at 25 °C. The numbers on the lines correspond to those in Table 2.

where ρ_{12} is the density of the solution, and w_2, the concentration of the polymer expressed by the weight fraction. The extrapolated values of $\bar{v}_{2,\mathrm{d}}$ at $w_2=0$, which are the main interest in this investigation, are summarized in the sixth column of Table 2.

The values of the partial specific refraction, $\bar{R}_{2,\mathrm{GD}}$, $\bar{R}_{2,\mathrm{LL}}$, and $\bar{R}_{2,\mathrm{Ey}}$, were calculated by fitting Eqs. (10), (11), and (12) to the data of n_1, dn/dc, and $\bar{v}_{2,\mathrm{d}}$. The results are shown in Table 2.

As may be seen in Table 2, the deviation of the partial specific refraction from the mean value in any particular solvent is smallest in the case of $\bar{R}_{2,\mathrm{LL}}$, and the specific refraction, $R_{2,\mathrm{He}}$ (=0.316, Eq. (7)) of bulk atactic poly(2-vinylpyridine) is in fair agreement with the averaged value of the partial specific refraction, $\bar{R}_{2,\mathrm{LL}}$ (=0.314, Eq. (11)). On the other hand, larger deviations are found with the corresponding specific refrac-

TABLE 2. PARTIAL SPECIFIC REFRACTION AND PARTIAL SPECIFIC VOLUME OF ATACTIC POLY(2-VINYLPYRIDINE) AT 25 °C

No.	Solvent	$R_{2,GD}$ Eq. (10)	$R_{2,LL}$ Eq. (11)	$R_{2,Ey}$ Eq. (12)	$\bar{v}_{2,}$ a)	$\bar{v}_{2,op}$ b)	$\frac{(\bar{v}_{2,op}-\bar{v}_{2,d})}{\bar{v}_{2,d}}\times 100$
5	*n*-Propanol	0.538	0.312	0.702	0.826	0.842	+1.9
6	Methanol	0.536	0.316	0.702	0.798	0.798	0
7	*n*-Buthanol	0.546	0.316	0.712	0.838	0.838	0
8	Ethanol	0.536	0.312	0.700	0.792	0.809	+2.1
10	Cyclohexanone	0.537	0.308	0.699	0.856	0.885	+3.4
16	Benzene	0.537	0.310	0.709	0.848	0.868	+2.4
17	Dioxane	0.553	0.319	0.721	0.882	0.869	−1.5
18	Methylethylketone	0.543	0.316	0.710	0.848	0.849	+0.1
	Mean	0.542 ±0.011	0.314 ±0.006	0.707 ±0.015			
		$R_{2,HD}$ Eq. (1)	$R_{2,He}$ Eq. (2)	$R_{2,Ey}$ Eq. (3)			
	Bulk a-P2VP	0.558	0.316	0.724			

a) $\bar{v}_{2,d}$=the values obtained densitometrically. b) $\bar{v}_{2,op}$=the values obtained optically.

tions of the bulk polymer, $R_{2,GD}$ (=0.558, Eq. (1)) and $R_{2,Ey}$ (=0.724, Eq. (3)), in comparison with the mean values of the partial specific refractions, $\bar{R}_{2,op}$ (=0.542, Eq. (10)) and $\bar{R}_{2,Hy}$(=0.707, Eq. (12)).

Of course, the specific refraction, R_2, is not necessarily the same as the partial specific refraction, $\bar{R}_2$; however, the agreement between $\bar{R}_{2,LL}$ and $R_{2,He}$ is a satisfactory indication of the applicability of the Heller's method in this polymer-solvent system.

The partial specific volume of the polymer, $\bar{v}_{2,op}$, in all the solvents used in this experiment was evaluated according to the graphical scheme described previously using the value of 0.316 for $R_{2,He}$ (=k). Examples in several solvents are illustrated in Fig. 3. The $\bar{v}_{2,op}$ values in all the solvents were also evaluated from Eq. (8); they agreed very closely with those obtained graphically.

The values of $\bar{v}_{2,op}$ thus obtained are summarized in the fifth and seventh columns of Tables 1 and 2 respectively. In the eighth column of Table 2 the percent deviation of $\bar{v}_{2,op}$ from $\bar{v}_{2,d}$ defined by $[(\bar{v}_{2,op}-\bar{v}_{2,d})/\bar{v}_{2,d}]\times 100$ is shown. Except for the solution in cyclohexanone, the percentage of deviation is less than 2.4; this is almost the same as the results for polystyrene reported by Heller,6) and this is also an indication of the validity of the application of the method of Heller to this polymer-solvent system.

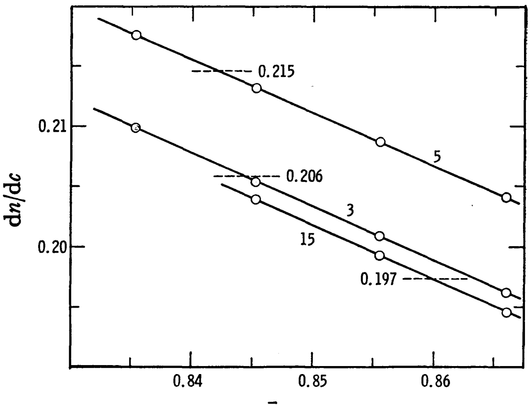

Fig. 3. Heller's plots for the tentative pairs of $\bar{v}_{2,op}$ and d*n*/d*c* obtained from Eqs. (5) and (7). The intersection of horizontal dashed lines with main plot gives $\bar{v}_{2,op}$ corresponding to experimentally obtained d*n*/d*c*. The numbers on the lines correspond to those in Table 1.

The values of Δ cited in the sixth column of Table 1 show the difference in $\bar{v}_{2,op}$ and the specific volume of bulk atactic poly(2-vinylpyridine), $v_{2,a}$ (=0.897 cm^3/g), defined by $\Delta=[(v_{2,a}-\bar{v}_{2,op})/v_{2,a}]\times 100$. As a whole, they are larger than those reported for polystyrene.6)

The specific volume, $v_{2,c}$ of the bulk crystalline isotactic poly(2-vinylpyridine) was 0.847 cm^3/g at 25 °C for a fraction ($M_W=8.7\times 10^4$). The difference in $v_{2,a}$ and $v_{2,c}$ may be attributed to the increase in the free volume of the amorphous polymer. The apparent absolute free volume of bulk poly(2-vinylpyridine), as defined by $[(v_{2,a}-v_{2,c})/v_{2,c}]\times 100$, is 5.90%, which is comparable to the value for polystyrene:6) 6.00—6.06%.

In the seventh column of Table 1 the apparent absolute free volumes of dissolved atactic poly(2-vinylpyridine), as defined by $\delta=[(\bar{v}_{2,op}-v_{,c})/v_{2,c}]\times 100$, are shown. Since the crystalline state is considered to be the most compact in the arrangement of the polymer segments, the negative values found in several solvents seem peculiar. The solvents which show negative values are 2-butanol, 1-propanol, 2-propanol, *n*-butanol, ethanol, and methanol, arranged in descending order of negative values. Even for a non-polar polymer such as polystyrene, a very small or slightly negative value of the apparent free volume in solution was pointed out by Heller,6) therefore, the extremely large negative values found for this polymer in ethanol and methanol are remarkable.

In order to explain the effect of the change in the values of $\bar{v}_{2,op}$ with the nature of the solvents, we considered first the thermodynamic interactions between the polymer and the solvent. For such a thermodynamic parameter,22) we used the values of $[(1/2-\chi_1)/V_1]$, where χ_1 is Flory's interaction parameter, and V_1, the molar volume of the solvent, as listed in the tenth column of Table 1. These values were obtained from the data of the limiting viscosity number for a fraction of atactic poly(2-vinylpyridine) ($M_W=28.7\times 10^4$) at 25 °C, assuming Flory's well-known expressions:23)

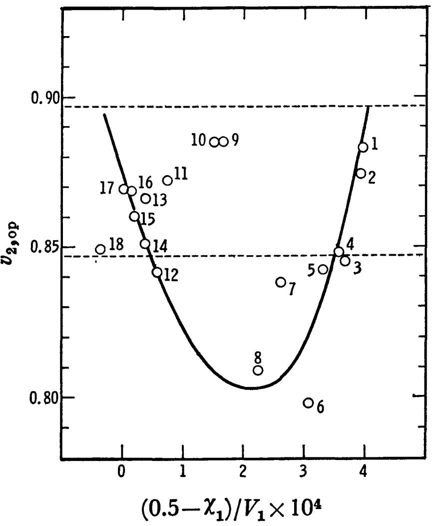

Fig. 4. Plots of the partial specific volume $\bar{v}_{2,\mathrm{op}}$ *vs.* thermodynamic parameter $(1/2-\chi_1)/\bar{V}_1$ at 25 °C. The numbers on the points correspond to those in Table 1. The upper and lower dashed lines correspond to the specific volumes, $v_{2,\mathrm{a}}$ and $v_{2,\mathrm{c}}$ of bulk atactic and bulk crystalline poly(2-vinylpyridine), respectively.

$$\alpha^5-\alpha^3=2C_m'(1/2-\chi_1)M^{1/2}$$

$$\alpha^3=[\eta]/[\eta]_\theta \qquad [\eta]_\theta=KM^{1/2}$$

They are cited in the ninth column of Table 1, while $\bar{v}_{2,\mathrm{op}}$ is plotted against them in Fig. 4. The points are rather scattered, some U-type relationship seems to exist between them. The shape of the curve is similar to that for the polystyrene-solvent system reported by Streeter and Boyer.22) The decrease in the $\bar{v}_{2,\mathrm{op}}$ with an increase in the solvent power may be attributed to the increase in the packing effect of the solvent molecules into the interior of the polymer coil because of the attraction between segments and solvent molecules.

As we have already shown, the interactions of poly(2-vinylpyridine) and alcohols, especially ethanol and methanol, are very strong because of the hydrogen-bonding formation.1,4,5) The anomalous light-scattering behavior of poly(2-vinylpyridine) in methanol has been explained in terms of the extremely strong solvation of methanol to the segment-forming wire netting.3) The peculiarity that the value of $\bar{v}_{2,\mathrm{op}}$ is smaller than that of $v_{2,\mathrm{c}}$ for isotactic crystalline poly(2-vinylpyridine) can also be attributed to this strong attraction between segments and solvents, which may result in a decrease in the partial specific volume of the solvent in addition to making for a closer packing of the solvent in the polymer coil.

The compressibility of the solvent molecule must also play an important role in such a case. In Fig. 5, $\bar{v}_{2,\mathrm{op}}$ is plotted against the values of the adiabatic compressibility, κ_s, at 25 °C and one atmosphere as cited in the eleventh column of Table 1. As may be seen in this figure, there is some tendency for the value of $\bar{v}_{2,\mathrm{op}}$ to decrease with an increase in the compressibility of the solvent. The compatibility of the large compressibility of methanol and ethanol and the large negative values of the apparent free volume of the polymer in these solvents are particularly remarkable.

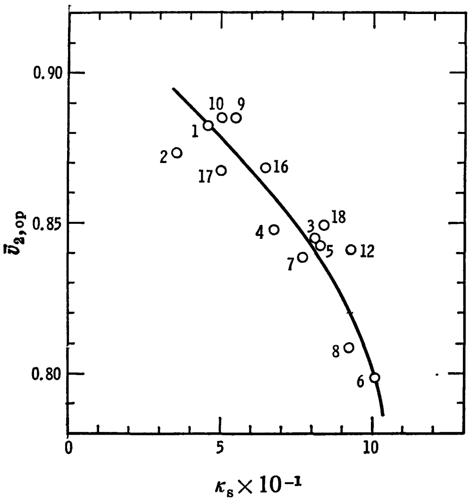

Fig. 5. Plots of the partial specific volume $\bar{v}_{2,\mathrm{op}}$ *vs.* adiabatic compressibility of solvent κ_s at 25 °C and 1 atmosphere. The numbers on the points correspond to those in Table 1.

The tendency for them to be a rapid increase in $\bar{v}_{2,\mathrm{op}}$ with an increase in $[(1/2-\chi_1)/\bar{V}_1]$ on the right-hand side of Fig. 4 is difficult to explain, but, it may be attributable to the crowding of the segments of different molecules in such a good solvent and to a decrease in the packing efficiency of solvent molecules. In addition, there may be some effects of the size and shape of the solvent molecule in their packing process. In Fig. 6, the values of $\bar{v}_{2,\mathrm{op}}$ are plotted against the value of the molar volume of the solvent molecule. Although there is no definite reciprocity between $\bar{v}_{2,\mathrm{op}}$ and V_1, some tendency for $\bar{v}_{2,\mathrm{op}}$ to increase with V_1 is shown by the line in Fig. 6. Here again, methanol and ethanol seem to be favorable for the packing in the polymer coil because of their small volume.

Finally, for the purposes of practical use in light-scattering measurements24,25) the empirical relation between dn/dc and n_1 for this polymer-solvent system was

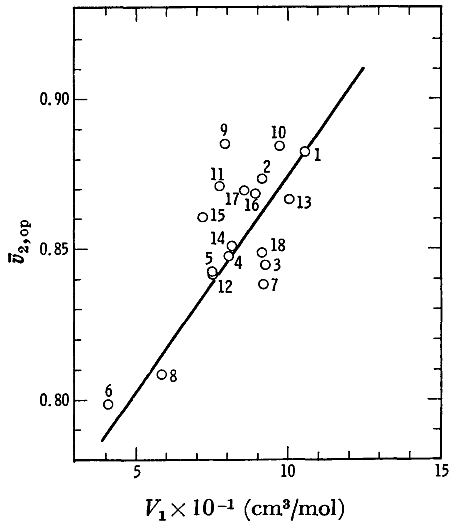

Fig. 6. Plots of the partial specific volume $\bar{v}_{2,\mathrm{op}}$ *vs.* molar volume of solvent V_1 at 25 °C. The numbers on the points correspond to those in Table 1.

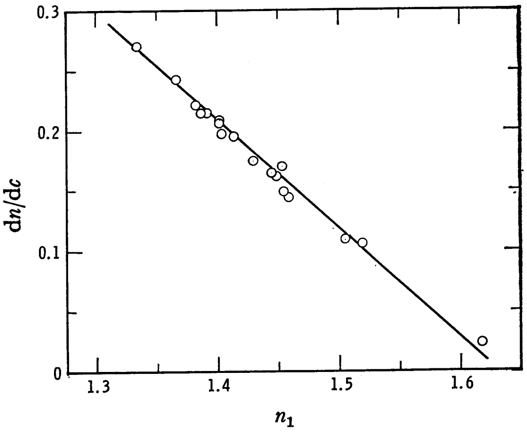

Fig. 7. Plots of specific refractive index increment dn/dc of atactic poly(2-vinylpyridine) *vs.* refractive index n_1 of solvent for 436 nm light at 25 °C.

evaluated. In Fig. 7 the values of dn/dc are plotted against the value of n_1 for 436 nm light. Their relation is represented by a linear line whose equation, as obtained by the least-squares method, is:

$$\mathrm{d}n/\mathrm{d}c = 0.900 \times (1.628-n_1) \qquad (13)$$

When volume additivity is assumed on the Gladstone-Dale expression for the specific refraction, Eq. (1) leads to this well-known equation:[26]

$$\mathrm{d}n/\mathrm{d}c = v_2(n_2-n_1) \qquad (14)$$

where each suffix is the same as before. The constants in Eq. (13), 0.900 and 1.628, agree well with the experimental values of $v_{2,\mathrm{a}}$ ($=0.897\ \mathrm{cm}^3/\mathrm{g}$) and n_2 ($=1.622$) presented previously.

Because the volume change on mixing the components in this polymer-solvent system is very remarkable, as has already been shown, the agreement between these values is clearly fortuitous; however, Eq. (13) can be used for predicting the value of dn/dc of atactic poly(2-vinylpyridine) within ±0.002 in a given solvent possessing the value of n_1.

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