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The Intrinsic Viscosity of Poly(4-vinylpyridine) of a Low Molecular Weight

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Synopsis. The intrinsic viscosities of poly(4-vinylpyridine) ($\bar{M}_n$: 1.37×10^3—9.67×10^4) were measured by use of various solvents. For every solvent, log[η]-log$\bar{M}_n$ plots gave lines with a slope of 1/2 in the region of low molecular weights ($\bar{M}_n \leq 10^4$). These lines were parallel to one another. This viscosity behavior was interpreted in terms of the influence of solvents on short-range interactions in the polymer chains.

Many studies[1] of the intrinsic viscosities of polymers have shown that, in a region of low molecular weights, the equation $[\eta]=K_0M^{1/2}$ holds in spite of measurements made using good solvents. Here, the constant, K_0, appeared to be independent of the kind of solvent; its value was near that of K_θ, namely, $K_0M^{1/2}\approx K_\theta M^{1/2}$. These experimental facts suggested the possibility of the evaluation of characteristic dimensions from viscosity measurements of polymers of low molecular weights in good solvents. However, the polymer–good solvent systems so far examined have been mainly nonpolar polymer–nonpolar solvent systems, and so the investigation of other systems, such as polar polymer–polar solvent systems, and a better-defined interpretation of the viscosity behavior described above were desired.

On the other hand, a theoretical treatment of the viscosities of short chains (polymers of low molecular weights) was reported by Perico and Rossi.[2] They showed, for some polymer–good solvent systems, that the intrinsic viscosities of short chains could be evaluated from the model of independent hindered rotation by introducing "thickness *b*" by a parameter.

In the present study, the poly(4-vinylpyridine)–good solvent system is adopted as a specific polymer–solvent system, in which strong polymer-solvent interactions are presented; this polymer–solvent system is a polar polymer–polar solvent system. For such a system the relation of [η]-*M* is examined, and the origin of the viscosity behavior of $[\eta]=K_0M^{1/2}$ is investigated by using the theory by Perico and Rossi.[2]

Experimental

Samples of poly(4-vinylpyridine) of various molecular weights were prepared by radical polymerization (monomer: 10 ml, chloroform: 50 ml, α,α'-azobisisobutyronitrile, 60 °C); the polymers were recovered by precipitation in petroleum ether. The average molecular weights of these polymer samples ranges from 1.37×10^3 to 9.67×10^4 (average degrees of polymerization, $\overline{DP}$: 13.1—921). The moleculat weights were determined using a "KUNAUAR vapor-pressure osmometer and membrane osmometer" in chloroform solutions at 37 °C; the vapor-pressure osmometric method was applied to polymer samples of $\bar{M}_n \leq 1.32\times10^4$, and the membrane osmometric method, to those of $\bar{M}_n \geq 1.32\times10^4$. For these samples, no fractionations were carried out. However, it would have no significant influence on the present discussion because the present investigation is concerned only with the discussion of the dependence of curves of [η] plotted against molecular weight on solvents.

The solvents used in the viscosity measurements were methyl alcohol, chloroform, and *t*-butyl alcohol. Ethyl methyl ketone/isopropyl alcohol (85/15 by wt) was also used as a relatively poor solvent (the expansion coefficient for the mixed solvent at 25 °C was evaluated as 1.06 in the viscosity study of poly(4-vinylpyridine) by Boyes and Strauss[3]). These solvent were purified by means of the usual method. The intrinsic viscosities were measured by use of the viscometers of the Ubbelohde type, the efflux times of which were 248.3, 214.1, 352.7, and 277.3 s for methyl alcohol, chloroform, *t*-butyl alcohol, and ethyl methyl ketone/isopropyl alcohol respectively. In the measurements, the temperature of water bath was maintained at 30±0.01 °C, and the efflux time was measured with a stopwatch reading to an accuracy of 0.1 s.

Results and Discussion

Plots of log [η] *against log M.* Figure 1 shows the plots of log [η] against log $\bar{M}_n$ for poly(4-vinylpyridine) in various solvents at 30 °C (the points for chloroform solutions fall on the line for methyl alcohol solutions; therefore, they are omitted in Fig. 1). In every case, the slope of the line decreases with a decrease in the molecular weight and becomes 1/2 in the region of molecular weights below 10^4.

For the poly(4-vinylpyridine)–good solvent system, as well as for the polymer–good solvent systems[1] examined previously, a slope of 1/2 is observed in the region of low molecular weights. However, the behavior of the lines with a slope of 1/2 is distinct from the previous observations[1] for various polymers; the lines with a slope of 1/2 for poly(4-vinylpyridine) are not concentrated on a line, but are parallel to one another.

The present data clearly indicate that the phenomenon of the slope of 1/2 is not associated with the θ state. The phenomenon should be attributed, rather, to the disappearance of long-range interactions resulting from the decrease in the molecular weights.

TABLE 1. INTRINSIC VISCOSITY FOR POLY(4-VINYLPYRIDINE) IN CH_3OH AT 30 °C

$\overline{DP}$ a)	N_c	R_s (Å)	[η] (dl/g) calculated	[η] (dl/g) measured
13.1	26	12.9	0.065	0.046
20.0	40	16.0	0.082	0.081
24.6	49	17.8	0.092	0.094
37.5	75	22.1	0.115	0.110
55.6	111	27.0	0.142	0.140
68.3	137	30.0	0.158	0.159
101	202	36.5	0.193	0.204

In calculations, $\Delta E=1.3$ kcal/mol, $b=4.8$ Å, and $\phi=2.87\times10^{21}$. a) Average degrees of polymerization.

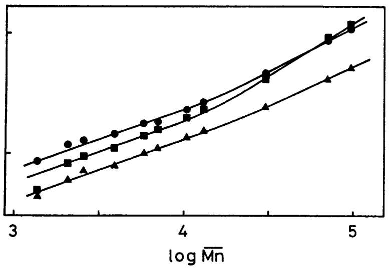

Fig. 1. Intrinsic viscosities of poly(4-vinylpyridine) in various solvents at 30 °C. ●: *t*-BuOH, ■: MeOH, ▲: EMK/*i*-PrOH (85/15 by wt).

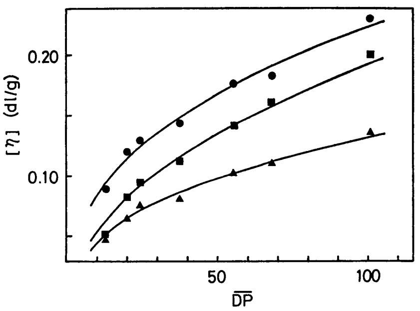

Fig. 2. Experimental viscosities and calculated curves by Eqs. 1 and 2. ●: *t*-BuOH, ■: MeOH, ▲: EMK/*i*-PrOH(85/15 by wt).

Table 2. The thickness (b) and energy (ΔE) for various solutions

Solvent	b (Å)	ΔE (kcal/mol)
MeOH	4.8	1.3
$CHCl_3$	4.8	1.3
t-BuOH	6.7	1.3
EMK/ *i*-PrOH	4.5	1.1

Intrinsic Viscosity of Polymers of Low Molecular Weights. According to the theory of Perico and Rossi[2] for short chains,

$$[\eta] = \phi 6^{3/2}(R_s^3/M), \tag{1}$$

$$R_s = (\langle S_0^2 \rangle)^{1/2} + b, \tag{2}$$

where the constant, b, is the "thickness" of the polymer chains. ϕ is a hydrodynamic parameter, and it takes an almost constant value (2.87×10^{21}) for the carbon-number of the backbone (N_c)>20. $\langle S_0^2 \rangle$ is the mean-square radius of gyration.

Table 1 shows the results of applying Eqs. 1 and 2 to poly(4-vinylpyridine) ($\bar{M}_n \leq 10^4$) in methyl alcohol. In the calculation, 2.87×10^{21} was used as the value of ϕ. $\langle S_0^2 \rangle$ was calculated by assuming an independent hindered rotation in the rotational-isomeric model; in Table 1, ΔE represents the energy of the gauche state relative to the trans in the model of independent hindered rotation. Figure 2 shows the experimental viscosities and calculated curves for the methyl alcohol, *t*-butyl alcohol, and ethyl methyl ketone (EMK)/isopropyl alcohol solutions (the points for chloroform solutions are omitted). Figure 2 indicates that the viscosities for the region of low molecular weights can be calculated by choosing the appropriate values of b and ΔE. The b and ΔE values yielding the best-fit curves are summarized in Table 2. The values of b are quite great (the size of the pyridine ring: about 3 Å), while the magnitudes of ΔE are acceptable.

The pyridine ring of poly(4-vinylpyridine) behaves as an electron donor, while methyl alcohol and chloroform can behave as electron acceptors. These solvents could be solvated to the polymer. *t*-Butyl alcohol is known to form hydrogen bonds with poly(4-vinylpyridine)[3] (*t*-butyl alcohol is the most bulky among the solvents used in the present experiments). The solvation power for ethyl methyl ketone/isopropyl alcohol is weaker than that for the other solvents in the present experiments. The solvation and hydrogen bonding must result in the increase in the values of b, and may be effective in the increase of ΔE.

The values of b and ΔE in Table 2 can be well interpreted by considering the solvation and hydrogen bonding (polymer-solvent interaction) described above. The viscosity data for any other polymer (low molecular weight)–good solvent system could also be explained in a similar manner.

On the basis of the above results and considerations, we can draw a conclusion regarding the polymers with low molecular weights (short chains) in solutions. The long-range interactions are ineffective in the polymers with low molecular weights. The conformations of the short chains are governed by the short-range interactions, in which polymer-solvent interactions are taken into account. The polymer-solvent interactions can be estimated in terms of b and ΔE. In the case of the systems in which the polymer-solvent interactions depend strongly on the solvents, parallel lines with a slope of 1/2 (this means $K_0 M^{1/2} \doteqdot K_\theta M^{1/2}$) are observed, and the dependence of b and ΔE on the solvents is detected.

The data for the poly(ethylene oxide) glycol-good solvent system[1,4] rather resemble the present observations. However, the polymer-solvent interaction in this system would be weak in comparison with that in the present system. As a result, the data were treated much like the data for various other polymer-good solvent systems.[1]

In the meantime, it has been pointed out, on the basis of various experiments[5] on polymers with low molecular weights, that the conformations and internal motion of short chains in solutions are somewhat different from those of polymers with high molecular weights. The conclusion derived in the present study would be useful for discussing such problems.

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