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Viscosity and light scattering studies of poly(4-vinylpyridine *N*-oxide) in solution

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Poly(4-vinylpyridine *N*-oxide) was synthesized and its chemical structure characterized by ultra-violet and nuclear magnetic resonance spectroscopies. The polymer was soluble in water and trifluoroethanol. The viscosity and light scattering behaviours of the polymer are similar to those often observed for polyelectrolytes, although the polymer contains no ionizable groups. The strong N–O dipole and the attendant interparticle electrostatic repulsion are believed to be the cause for the unusual solution behaviour. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(4-vinylpyridine *N*-oxide); viscosity; light scattering)

INTRODUCTION

In the course of our study of water-soluble polymers, we synthesized poly(4-vinylpyridine *N*-oxide) (PVPNO). The synthesis of the polymer was reported almost two decades ago, yet there was little systematic information about its structure, characterization and solution properties. Although the polymer contains no ionizable groups and hence is not a polyelectrolyte, charge separation across the N–O bond has been known to result in a large dipole moment[1]. In the case of PVPNO solution, this apparently gives rise to viscosity and light scattering characteristics often associated with the 'polyelectrolyte' effect. Our preliminary findings are reported in this paper.

EXPERIMENTAL

Synthesis

The synthetic procedure for poly(4-vinylpyridine *N*-oxide) (PVPNO) is shown in *Scheme 1*.

Poly(4-vinylpyridine). The monomer 4-vinylpyridine was purchased from Aldrich Co. and distilled to remove the inhibitor before use. 2,2′-Azobisisobutyronitrile was purified by recrystallization in methanol and dried in a vacuum oven overnight at room temperature. It was added to 4-vinylpyridine at a concentration of $8.2 \times 10^{-1}\,\mathrm{g\,ml^{-1}}$ and the solution was subjected to a 'freeze–thaw' cycle three times to remove the dissolved oxygen. Polymerization proceeded at 70 ± 2°C for 20 min under vacuum. Methanol was then poured into the flask to terminate the reaction. Poly(4-vinylpyridine) (P4VP), which was soluble in methanol, was then precipitated in water. The precipitate was redissolved in ethanol and precipitated in water three times and dried in vacuum at 60°C for three days. The yield was at least 85%.

Poly(4-vinylpyridine N*-oxide).* The synthetic procedure was the same as the one described in the literature for the oxidation of poly(2-vinylpyridine)[2]. First, 60 g P4VP in 300 ml glacial acetic acid was heated at 75–80°C for 24 h, with the addition of 150 ml of 30% hydrogen peroxide. After the solvent was removed by distillation in vacuum, the polymer was dissolved in water to which Amberlite IRA-400 ion-exchange resin was added. The *N*-oxide polymer, PVPNO, was precipitated in ethanol. Residual solvent trapped in the precipitate was extracted by methanol in a continuous extractor for three days. The polymer was dried in a vacuum oven at 60°C for two days. The yield was >80%.

Characterization

Intrinsic viscosity. An Ubbelohde viscometer was used to determine the intrinsic viscosity [η], of poly(4-vinylpyridine) and poly(4-vinylpyridine *N*-oxide) in a thermostated water bath which was kept at 25 ± 0.1°C. Ethanol was used as the solvent for P4VP, while water and trifluoroethanol were used for PVPNO.

Infra-red spectra. An Analect FX 6260 Fourier-transform infra-red (*FT*i.r.) spectrometer was used to identify the functional groups of poly(4-vinylpyridine) and PVPNO.

Ultra-violet spectra. A Varian Gary 210 ultra-violet spectrometer was used to determine the u.v. absorption of poly(4-vinylpyridine *N*-oxide).

Nuclear magnetic resonance spectra. A General Electric GN-300 Fourier-transform nuclear magnetic resonance spectrometer operating at 300 MHz was used

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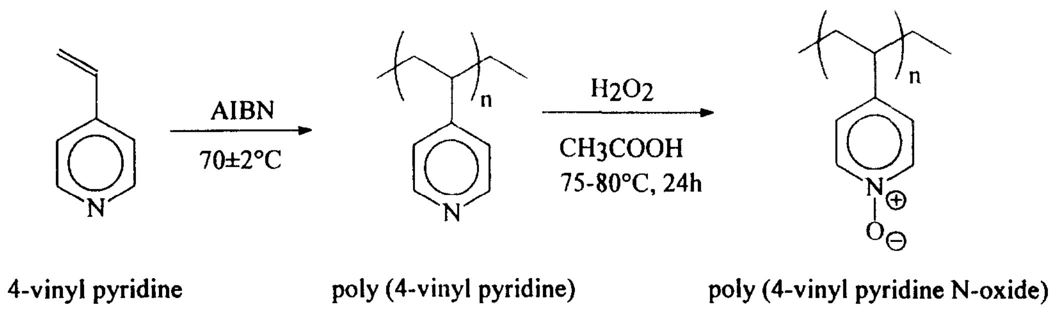


Scheme 1

to verify the structure of PVPNO in both the solid and the liquid states. ^{13}C and ^{1}H n.m.r. were examined at room temperature.

Glass transition temperature. The glass transition temperatures (T_g) of all samples were determined with the use of a DuPont 9900 Thermal Analyzer with a Differential Scanning Calorimeter Module (d.s.c.). The sample was dried in a vacuum oven at 60°C at least overnight prior to measuring the T_g. Typically, the heating rate was $20°C\,min^{-1}$ and the scanning range was from −50 to 200°C.

Thermogravimetric analysis. Thermogravimetric analysis was conducted with a DuPont 9100 Thermal Analyzer with a Thermogravimetric Analysis Module (t.g.a.). The typical sample amount was about 8 mg and the heating rate was $20°C\,min^{-1}$ from 40 to 400°C.

Wide-angle X-ray diffraction. A Philips 3100 X-ray generator with an APD-3720 diffractometer was used to analyse the diffraction pattern of the polymer. A powdered sample was placed on a glass slide, which was coated with a thin layer of grease to affix the powder. The diffraction pattern was taken in the range of 5 to 50° at $0.2°\,min^{-1}$.

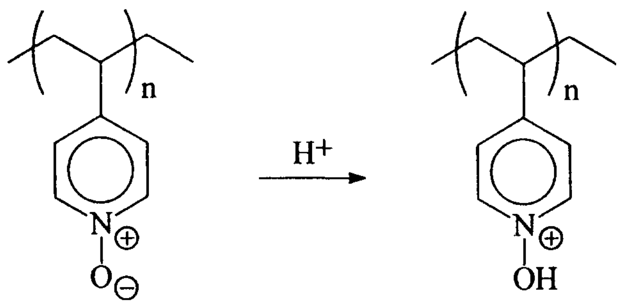
pH measurement. pH measurement was conducted with a Fisher Accumet® pH meter, model 805 MP. The pH meter was calibrated by using pH 4.00 and pH 7.00 buffer solutions as primary standards at ambient temperature.

Small-angle light scattering measurement. Small-angle light scattering measurements were conducted with a KMX-6 low-angle light scattering photometer (Chromatix-LDC/Milton Roy) at a wavelength of 633 nm. The specific refractive index increment, dn/dc, was measured with a KMX-16 differential refractometer at 25 ± 0.1°C. The solvents were first filtered by a 0.1 μm filter twice. The aqueous solution was filtered by 0.2 μm and 0.45 μm filters three times each, then flowed through 0.45 and 0.2 μm filters into the quartz cell directly. The trifluoroethanol solution was filtered by 0.45 μm filter four times, then flowed through 0.45 μm filter into the quartz cell directly.

RESULTS AND DISCUSSION

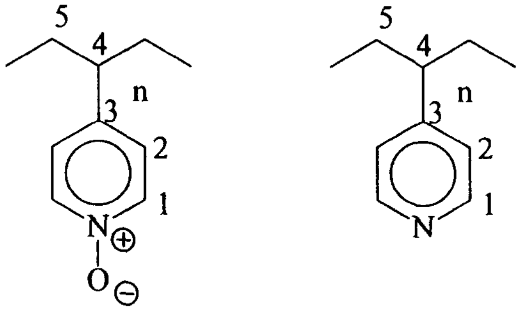
Characterization of chemical structure

Complete removal of acetic acid is crucial to the characterization of polymer structure since the *N*-oxide polymer was thought to assume the protonated form in acidic solvents according to the following reaction[3]:



Recently, Arai[4] reported that poly(4-vinylpyridine *N*-oxide) refluxed in acetic acid at a higher temperature (at 150°C for 5 h) would rearrange to poly(4-vinyl-2-hydroxypyridine). The three isomers can be easily distinguished by their u.v. spectra. The characteristic peaks are listed in *Table 1*. Our u.v. absorption peaks are in complete accord with those of the model compound, 4-methylpyridine *N*-oxide.

The ^{13}C and ^{1}H n.m.r. chemical shifts in solution are shown in *Tables 2* and *3*. The ^{13}C n.m.r. chemical shifts of poly(4-vinylpyridine *N*-oxide) in the solid state agree with the chemical shifts in solution. The carbons of P4VP and PVPNO are numbered as shown below:



Poly(4-vinylpyridine *N*-oxide) was also characterized by i.r. spectroscopy. There are two peaks at 1238 and $1200\,cm^{-1}$ respectively, which are typical of 4-substituted pyridine *N*-oxide compounds[5]. In particular, the $1238\,cm^{-1}$ peak can be attributed to the vibration mode of the N–O bond.

The molecular weight of PVPNO was at first

Table 1 Characteristic peaks of u.v. absorption in water

	Poly(4-vinylpyridine *N*-oxide)	Protonated 4-methylpyridine *N*-oxide	Poly(4-vinyl-2-hydroxypyridine)	4-Methylpyridine *N*-oxide
Absorption peaks (nm)	205, 257	226, 254	~230	206, 256
Molar extinction coefficient, ϵ	19844 at 257 nm	2700 at 254 nm	–	14300 at 256 nm

Table 2 ^{13}C chemical shifts of poly(4-vinylpyridine) and poly(4-vinylpyridine *N*-oxide) dissolved in deuterium oxide; all chemical shifts are based on internal standards tetramethylsilane (TMS) and DSS

	C1	C2	C3	C4 and C5
Poly(4-vinylpyridine)	148.96	122.27	152.96	40
Poly(4-vinylpyridine *N*-oxide)	141.11	128.94	151.65	42.66–44.55

Table 3 ^1H chemical shifts of poly(4-vinylpyridine) and poly(4-vinylpyridine *N*-oxide) dissolved in deuterium oxide; all chemical shifts are based on internal standards TMS and DDS (m means multiplicity)

	H on C4 and C5	H on C1	H on C2
Poly(4-vinylpyridine)	1.6, m	6.6, m	7.02, m
Poly(4-vinylpyridine *N*-oxide)	1.8, m	8.2, m	8.0, m

estimated from the intrinsic viscosity measurement of the precursor. The intrinsic viscosity of poly(4-vinylpyridine) was 0.776 dl g^{-1}. From the Mark–Houwink equation:

$$[\eta] = K(\bar{M}_v)^a$$

where $K = 2.5 \times 10^{-2}$ ml g^{-1} and $a = 0.68$ in ethanol solvent[6], the viscosity-average molecular weight was calculated as 1.36×10^5. The viscosity-average molecular weight of poly(4-vinylpyridine *N*-oxide) was then estimated as 1.57×10^5, if all the poly(4-vinylpyridine) had been transformed to PVPNO without degradation or fractionation. However, as will be seen later, the molecular weight of PVPNO determined by light scattering measurements was much smaller.

Physical properties

Thermal analysis. The T_g of the precursor, poly(4-vinylpyridine), was determined by d.s.c. to be 153°C, and the value was close to the reported T_g of 146°C[6]. The T_g of poly(4-vinylpyridine *N*-oxide), however, was not readily identifiable by d.s.c. prior to degradation and there was no literature value.

In t.g.a. experiments, the onset decomposition temperature of PVPNO was located at 264°C. During the first stage of weight loss, the sample weight was reduced by 41.15%. This value agrees with literature data[7].

X-ray diffraction. No crystallinity was detected in the X-ray diffraction pattern.

Acidity of PVPNO aqueous solution. The pH value of a 1% PVPNO solution in deionized water was measured. To our initial surprise, the solution was weakly acidic, with a pH value of 3.42. The measurements were repeated on different days with several freshly prepared solutions and the results remained the same. The pH value agrees with literature data on organic compounds bearing N–O groups[8]; however, we were unable to find an explanation in the papers perused by us.

Viscosity. PVPNO was found to be soluble in water and acidic media but insoluble in most organic solvents including dimethylsulfoxide (DMSO), dimethylacetamide (DMAc), tetrahydrofuran (THF) and acetone. The dilute-solution viscosity data of PVPNO in water are shown in *Figure 1a*, in which the reduced viscosities are seen to change only slightly at concentrations greater than 0.2 g dl^{-1} but increase sharply upon dilution from that concentration. The shape of the curve is similar to those often found for polyelectrolytes. In the case of polyelectrolytes, increased dilution allows the counter-ions to distribute themselves at larger distances from the polyion; the attendant reduction in the shielding of fixed charges causes the polyion to expand. Although the reduced viscosities of PVPNO also increase upon

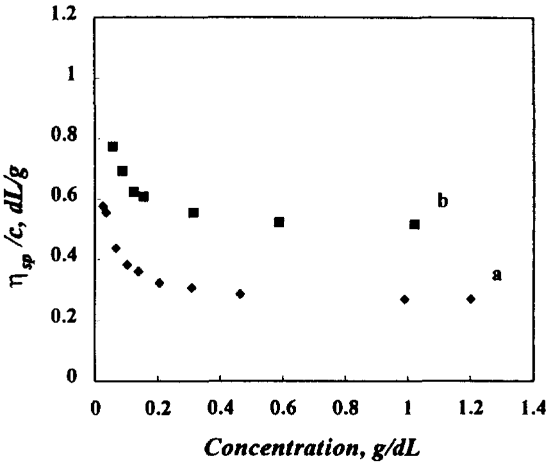


Figure 1 Reduced viscosity of PVPNO: (a) in water; (b) in TFE

dilution, the underlying cause is likely to be different. Nevertheless, we have replotted the viscosity data in accordance with the Fuoss equation[9], which is satisfactory in correlating polyelectrolyte viscosity data in many cases. However, our results do not conform to the linear relation between $(\eta_{sp}/c)^{-1}$ and $c^{-1/2}$ predicted by equation (1):

$$\frac{\eta_{sp}}{c} = \frac{A}{1 + B\sqrt{c}} \tag{1}$$

Instead, the data are better represented by the following equation (2):

$$\left(\frac{\eta_{sp}}{c}\right) - \left(\frac{\eta_{sp}}{c}\right)_{\infty} = \frac{A}{c + B} \tag{2}$$

where $(\eta_{sp}/c)_{\infty}$ is the limiting value of η_{red} at high concentrations. A plot of η_{sp}/c vs. $1/(c + B)$ is shown in *Figure 2a*, in which B is taken as $0.0021\,\mathrm{g\,dl^{-1}}$. The intercept at the ordinate axis gives $(\eta_{sp}/c)_{\infty}$ as $0.26\,\mathrm{dl\,g^{-1}}$, in agreement with experimental data at high concentrations.

Since it is well known that the viscosity of an aqueous polyelectrolyte solution is often strongly influenced by added salts, we have carried out a set of experiments in which LiCl was added to the aqueous solution. Even a small amount of LiCl (0.037%) sufficed to eliminate the upswing of reduced viscosity at high dilutions (*Figure 3*).

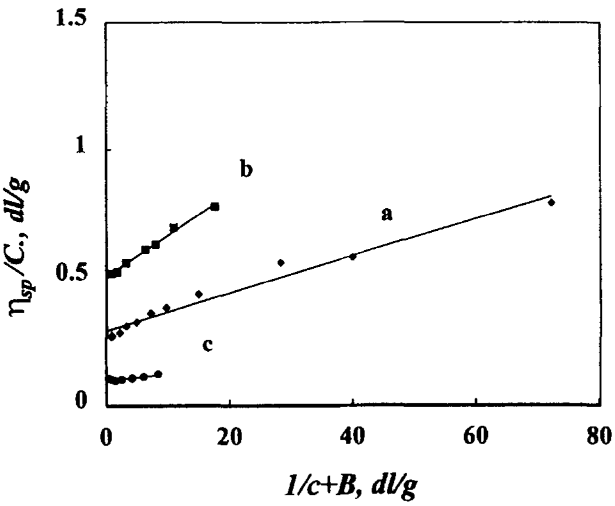


Figure 2 Plot of η_{sp}/c vs. $1/(c + B)$: (a) PVPNO in water; (b) PVPNO in TFE; (c) halatotelechelic ionomer in DMF

In our search for an organic solvent for PVPNO, we found the polymer to be readily soluble in trifluoroethanol (TFE). The hydroxyl group in TFE is acidic and the dissolution of PVPNO in TFE is in line with its solubility in other acidic media. As in the case of aqueous solution, the reduced viscosities in TFE remained nearly unchanged at $c > 0.3\,\mathrm{g\,dl^{-1}}$ but increased sharply when the solution concentrations were decreased (*Figure 1b*). Again, the data fall on a straight-line plot predicted by equation (2) with an intercept of $0.50\,\mathrm{dl\,g^{-1}}$ (*Figure 2b*) and an assumed B value of $0.0035\,\mathrm{g\,dl^{-1}}$. In this connection we noted that the same linear relation fitted the viscosity data of a halatotelechelic ionomer in a polar solvent[10], dimethylformamide (DMF) (*Figure 2c*). Hara and coworkers argued that the essential factors causing the polyelectrolyte behaviour were intermolecular rather than intramolecular interactions, since the ionic groups in halatotelechelic ionomers were located only at chain ends. This view was elaborated further by Hara in the interpretation of the results of light scattering measurements of ionomer solutions[11].

Light scattering. The results of small-angle light scattering experiments are plotted in *Figure 4*. In the figure, R_0 is the excess reduced scattered intensity at $\theta \approx 0$, K is defined as $4\pi^2\lambda_0^2(\mathrm{d}n/\mathrm{d}c^2/N_A\lambda^4$ for a polarized incident beam, and the terms n_0, $\mathrm{d}n/\mathrm{d}c$, N_A and λ have their usual meanings. It can be seen that the reciprocal reduced scattered intensity in water increases sharply with concentration at low c values and then bends over and levels off at high concentrations. The results obtained in TFE show similar trends. When Kc/R_θ values were expressed as a polynomial of c, the intercept at zero concentration was obtained as 2.30×10^{-5} (or $MW = 43\,000$) in water solution and 2.07×10^{-5} ($MW = 48\,000$) in TFE solution. Note that the molecular weights so determined are much smaller than that of the P4VP precursor estimated from the Mark–Houwink equation. We believe that a major contributor to the discrepancy is the removal of high-molecular-weight material in the repeated filtration steps employed prior

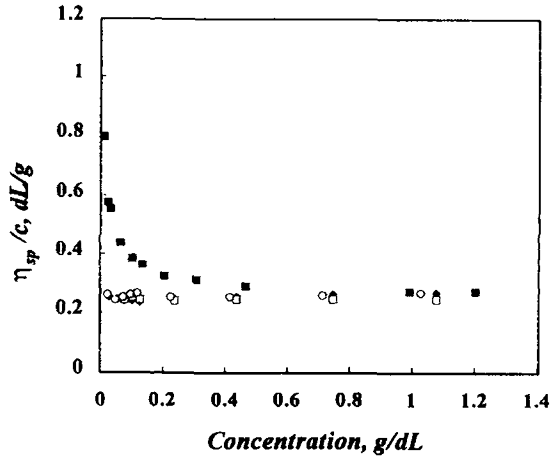


Figure 3 Reduced viscosity of PVPNO in LiCl aqueous solution: (■) without LiCl; (◆) 0.037% LiCl; (□) 0.327% LiCl; (○) 3.154% LiCl

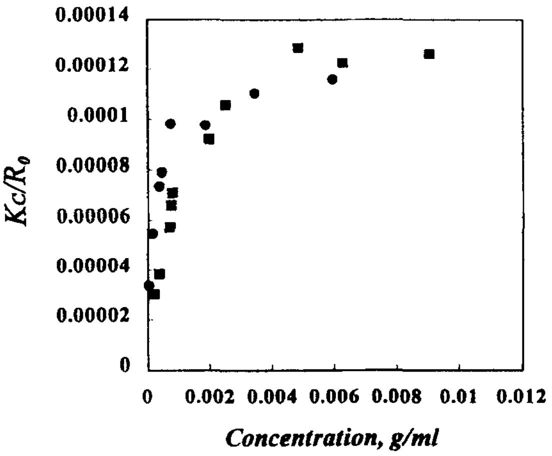


Figure 4 Reduced scattering intensity of PVPNO: (●) in water; (■) in TFE

to the light scattering measurements. This was proved by checking the u.v. absorption of the solution after every filtration step. After being passed through a 0.45 μm filter the first time, the solution decreased in concentration by about 49%; a second pass, through a 0.2 μm filter, decreased the concentration by another 4%. Subsequent filtration did not change the concentration materially even after 10 passes through 0.2 μm filters.

The shape of the reduced scattering intensity curves in *Figure 4* is again common to polyelectrolytes. Similarly shaped curves were reported by Doty and Steiner[12] in 1952 for serum albumin and for poly(methacrylic acid) in water, and more recently by Hara *et al.* for sodium salts of lightly sulfonated polystyrene in DMF. The interpretation of our results makes use of the analysis developed by them. The equation used by these authors was the general expression derived by Zernicke and Prins for the loss in scattering power per particle:

$$R_\theta = KcMP(\theta)\left(1 - \frac{4\pi N}{V}\int_\theta^\infty [1-\rho(r)]\frac{\sin(qr)}{qr}r^2\,\mathrm{d}r\right) \tag{3}$$

where $P(\theta)$ is the particle scattering factor, $\rho(r)$ is the radial distribution function of particles, q is the scattering vector $4\pi \sin(\theta/2)/\lambda$, and N is the number of particles in volume V. The first term on the right-hand side of equation (3) represents the scattering from a single particle; in our measurements at small angles, $P(\theta) \approx 1$. The second term describes the loss of scattering due to external interference arising from interparticle interaction. The integral in equation (3) was evaluated by Doty and Steiner using several interparticle potential functions for $\rho(r)$. The simplest model to be used in the following is the hard-sphere model, for which equation (3) can be simplified, for small q, to:

$$\frac{Kc}{R_\theta} = \frac{1}{M}\left(1 + \frac{4\pi N D^3}{3M}c\right) \tag{4}$$

where D is the effective diameter of the sphere. It is obvious from the shape of the reduced scattering intensity curve that D is a decreasing function of solution concentration. The effective diameter D_0 in the limit of zero concentration was calculated from the initial slope of the curve, which was obtained by curve fitting with a polynomial as mentioned before. The D_0 values are 50.8 nm in water and 38.3 nm in TFE.

If an electrostatic repulsion potential[9] is used:

$$\psi(r)/kT = \ln[1 - \exp(-r/r_0)^2]^{-2} \tag{5}$$

the light scattering equation for small q becomes:

$$\frac{Kc}{R_\theta} = \frac{1}{M}\left(1 + 1.164\pi^{3/2}\frac{N_0}{M}r_0^3 c\right) \tag{6}$$

The r_0 values calculated by the use of equation (6) are 45.8 nm for water and 34.8 nm for TFE solutions, respectively.

The effective diameter D is a measure of the distance of closest approach of centres of the particles, and the large magnitude calculated above signifies a strong repulsion effect between particles. The value of D is not the same as the chain dimension, which depends on the molecular weight and chain flexibility, and is not simply related to the root-mean-square end-to-end distance of the chain, R[13]. In other words, the relationship between D and R cannot be represented by a simple proportional constant. In Hara's study on sodium salts of partially sulfonated polystyrene in DMF, the D_0 value is 220 nm for a polymer having a *MW* of 4×10^5 and an ion content of 4%. The large magnitude of D_0 for the polystyrene ionomer is to be compared with the corresponding value of 42 nm for the precursor. In the case of poly(4-vinylpyridine *N*-oxide) in water and trifluoroethanol, regardless of the model used, the large D_0 or r_0 values, when compared with the contour length of 55–61 nm, are consistent with strong interparticle forces due to dipole interaction being operative in the system.

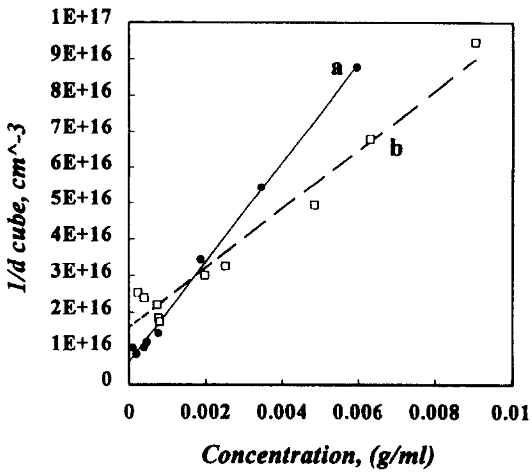


Figure 5 Effective diameter vs. concentration based on equation (7): (a) in water; (b) in TFE

The higher viscosities of PVPNO in TFE indicate that TFE is a better solvent compared with water, and that the PVPNO molecules can be more efficiently solvated by TFE. Therefore, the chain dimension in TFE is probably larger than that in water.

On the other hand, the effective hard-sphere diameter of poly(4-vinylpyridine *N*-oxide), which is not necessarily related to chain dimension, is about 20% larger in water than in trifluoroethanol. It is possible that trifluoroethanol is slightly acidic and the hydroxy group interacts to some degree with the *N*-oxide group. Consequently, the dipole interaction of the whole polymer chain is affected and the interparticle interference is smaller.

The hard-sphere and electrostatic repulsion models predict similarly shaped scattering curves. We have followed Doty's method of fitting the entire curve by employing the hard-sphere model with the additional assumption that D^3 is inversely related to c, as in equation (7):

$$1/D^3 - 1/D_0^3 = gc \tag{7}$$

The proportionality constant g was estimated by using the D_0 value previously calculated from the initial slope and by choosing an appropriate D value, according to equation (7), from the plateau region of the scattering curve. The calculated results are shown in *Figure 5*.

CONCLUSION

The viscosity and light scattering data of PVPNO show typical polyelectrolyte-like behaviour, although the polymer contains no ionizable groups. The results were discussed in terms of intermolecular interaction due to the presence of a strong dipole in the PVPNO segment.

ACKNOWLEDGEMENTS

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