Polymer complexes: 25. Complexing ability of poly(5-vinylsalicylidene-2-aminopyridine) towards different metal(II) salts

Adel Z. El-Sonbati*, Ashrafe A. El-Bindary and Mostafa A. Diab
Department of Chemistry, Faculty of Science, Mansoura University, Demiatta, Egypt

and Mohamed A. El-Ela and Sami A. Mazrouh
Department of Chemistry, Faculty of Engineering, Zagazig University (Banha Branch), Egypt
(Received 18 December 1992; revised 15 April 1993)

Mononuclear and binuclear complexes of poly(5-vinylsalicylidene-2-aminopyridine)† were prepared by the reaction of the homopolymer with copper(II), cobalt(II), nickel(II), cadmium(II), dioxouranium(VI) and palladium(II) salts. Metal(II) acetates and palladium chloride were found to give mononuclear complexes, while cupric chloride gave a binuclear complex. The polymer complexes have been characterized on the basis of elemental analysis, u.v. and i.r. spectroscopy, and magnetic susceptibility measurements. The stereochemistry and the nature of the complexes are markedly dependent upon the molar ratios of the reactants, the pH of the system and the nature of the anions involved. In all of the complexes the homopolymer was chelated to the metal ion through the nitrogen atom of the azomethine group and the oxygen atom of the phenolic group. The low value of the magnetic moment of the binuclear copper complex is due to an antiferromagnetic interaction between two adjacent copper atoms. The ligand field parameters have been calculated and related to the electronic environments. The electronic absorption of the homopolymer was investigated in organic solvents of varying polarities and buffer solutions of different pH, and the behaviour in the latter has been utilized in calculating the pK_a of the phenol group.

(Keywords: polymer complexes; metal salts; electronic spectra)

INTRODUCTION

Oxygen-bridged homo- and hetero-binuclear complexes have attracted great attention as a result of their interesting spectroscopic and magnetic properties, and their use in biochemical processes and homogeneous catalysis[1-3]. El-Dissouky and El-Sonbati[1] used mononuclear bis(phenyl-2-picolylketonato) copper(II) as the ligand and prepared a series of binuclear and trinuclear complexes containing this species. The objective of the present work is to prepare functionalized polymers with chelating groups and to investigate their complexing abilities towards transition metals. In this paper we have prepared binuclear complexes by the direct reaction of 5-vinylsalicylidene-2-aminopyridine and cupric chloride. Characterization of the latter complex has been carried out in a comparative study involving the corresponding mononuclear complexes.

EXPERIMENTAL

Materials

Salicylaldehyde (Aldrich) was degassed twice, distilled on a vacuum line, and stored over anhydrous Na_2SO_4. Paraformaldehyde and 2-aminopyridine (Merck) were used without further purification, and 2,2'-azobisisobutyronitrile (AIBN) (Eastman Kodak) was purified by recrystallization from ethanol[4].

Preparation of 5-vinylsalicylidene-2-aminopyridine

The 5-vinylsalicylidine-2-aminopyridine (VSP) monomer was prepared according to the method of El-Sonbati[5-7] in a yield of 60%. Calculated for $C_{14}H_{12}N_2O$ ($M=224$) requires: C 75.09, H 5.39 and N 12.52; found C 75.21, H 5.41 and N 12.50%.

Preparation of poly(5-vinylsalicylidene-2-aminopyridine) (PVSP) homopolymer and polymer complexes of 5-vinylsalicylidene-2-aminopyridine (VSP) with various transition metal salts

VSP was polymerized in dimethylformamide (DMF) by refluxing for 6 h with AIBN as the initiator[5-8]. The polymer product was precipitated by pouring into distilled water. The PVSP polymer has been characterized elsewhere[8] by its limiting viscosity number and number-average molecular weight.

Polymer complexes were prepared by the reaction of VSP (0.01 mol) in DMF (20 cm^3) and various metal salts (0.01 mol) in DMF (25 cm^3) with 0.1 w/v AIBN as the initiator. The mixture was heated under reflux for 6 h and the resulting polymer complexes were precipitated by adding the mixture to a large excess of distilled water

* To whom correspondence should be addressed. Present address: Department of Chemistry, Faculty of Science, Sana'a University, PO Box 13764, Yemen
† Systematic name: poly[2-(5-vinylsalicylidenimino)pyridine]

0032-3861/94/030647-06

Table 1 Analytical data obtained for the PVSP homopolymer and its metal chelates

Compound[a]	Expt. (Calc.) (%)				μ (μ_B)[b]	Decomposition temperature (°C)	Yield (%)
	C	H	N	Metal			
PVSP						870	70
VSP–$CuCl_2$[c]	52.17	3.40	8.80	20.00	1.59	300	80
	(52.01)	(3.42)	(8.69)	(19.73)			
VSP–CuX_2	65.70	4.30	10.99	12.20	1.89	305	75
	(65.90)	(4.32)	(11.00)	(12.47)			
VSP–CoX_2	66.60	4.40	10.80	11.62	4.46	320	78
	(66.54)	(4.36)	(11.09)	(11.67)			
VSP–NiX_2	66.51	4.40	10.91	11.70	d	310	74
	(66.57)	(4.36)	(11.00)	(11.63)			
VSP–CdX_2	60.31	4.00	10.20	20.40	d	350	72
	(60.17)	(3.93)	(10.03)	(20.13)			
VSP–$PdCl_2$	61.90	3.89	10.31	19.00	d	360	75
	(60.83)	(4.00)	(10.14)	(19.26)			
VSP–UO_2X_2	47.00	3.01	8.01	32.73	d	315	76
	(46.93)	(3.10)	(7.82)	(33.21)			

[a] X is acetate ion

[b] Value given is per metal ion, measured at room temperature; d is diamagnetic

[c] Chlorine content was determined by combustion of the solid complex (30 mg) in an oxygen flask in the presence of a KOH/H_2O_2 mixture, followed by titration with a standard $Hg(NO_3)_2$ solution using diphenylcarbazone as the indicator[2]

containing a small amount of hydrochloric acid, the latter to remove any unreacted metal salts. Both the PVSP and the polymer complexes were filtered, washed with water and dried in a vacuum oven at 40°C for several days.

Measurements

Microanalysis of all of the samples was carried out at Cairo University Analytical Centre, with the metal contents of the complexes being calculated by a standard technique[5–7] (see *Table 1*). ^{1}H n.m.r. spectra were obtained with a Jeol FX90 Fourier transform spectrometer with DMSO-d_6 as the solvent and TMS as the internal standard. I.r. spectra were recorded on a Perkin–Elmer 1340 spectrophotometer, with u.v.–vis. spectra being measured (nujol mull) on a Pye Unicam 8800 spectrophotometer. Magnetic measurements were carried out at room temperature by using Gouy's method, employing $Hg[Co(SCN)_4]$ for calibration purposes, and were corrected for diamagnetism by using Pascal's constant.

RESULTS AND DISCUSSION

Characterization of the homopolymer

Both i.r. and ^{1}H n.m.r. spectroscopy were used to characterize the PVSP homopolymer. The i.r. spectrum of the new ligand (see *Table 2*) exhibits absorptions due to the pyridine ring, the –C=N and OH groups and the phenyl ring. The spectrum was characterized by one strong band at 1636 cm^{-1}, which was assigned to the C=N stretching vibration of the PVSP linkage[5,6]. In the spectrum of PVSP, seven prominent bands due to pyridine-ring vibrations are observed at 1585, 1558, 1460, 1435, 1000, 625 and 425 cm^{-1}. The first four of these are due to the C=C and C=N modes[7,9], the 1000 cm^{-1} band is due to ring breathing and the last two are due to ring deformation[7,10]. The donation of electrons by the nitrogen atom of the pyridine will increase the double bond character of the C=C and C=N bonds because the pull of electrons away from hydrogen is directed towards these bonds. In addition, the PVSP spectrum shows no absorption bands in the 3400 cm^{-1} region which might be assigned to a free OH-stretching vibration. Instead, broad bands of intermediate intensities appear at 2900–3400 cm^{-1} indicating the presence of hydrogen bonds as part of a resonating ring system[5–7]. Strong bands occurring at 1370 and 1520 cm^{-1} are assigned to C–N and C–O, respectively. As a result of electron delocalization towards the benzene ring, the phenolic C–O stretch is expected to occur at higher energy levels.

Table 2 I.r. frequency data (cm^{-1}) obtained for the PVSP homopolymer and its metal chelates

Compound[a]	ν_{OH}	$\nu_{C=N}$	ν_{C-O}
PVSP	2900–3400	1636	1530
VSP–$CuCl_2$	–	1613	1555
VSP–CuX_2	–	1625	1535
VSP–CoX_2	–	1630	1540
VSP–NiX_2	–	1628	1538
VSP–CdX_2	–	1620	1540
VSP–$PdCl_2$	–	1622	1537
VSP–UO_2X_2	–	1620	1541

[a] X is acetate ion

The ^{1}H n.m.r. spectrum of PVSP in DMSO-d_6 exhibits signals at 6.4–8.9, 9.2, and 9.9–10.5 ppm, representing aromatic and pyridine ring protons, HC=N protons, and phenolic group protons, respectively. This 'downfield phenomenon' is attributed to the existence of hydrogen bonding in PVSP[7]. The signals at 167.56, 144.5, 146.89 and 135.56–121.78 ppm, respectively, which are observed in the ^{13}C n.m.r. spectrum of PVSP, are assigned to the

carbons attached to the oxygen, methyne, pyridine atoms and phenyl carbons. The first three signals are due to a considerable use in the position of carbon attached to the different participating groups[11].

Characterization of the polymer complexes

All of the complexes were air-stable, non-hygroscopic solids, which decomposed at high temperatures and were found to be insoluble in common organic solvents. The stoichiometries of the complexes have been deduced from their elemental analysis results. These indicate that the copper (II) complexes fall into two distinct categories. The reaction of metal acetates with the VSP monomer gives compounds with formulae which correspond to $[M(VSP-H)_2]_n$, while the reaction of $CuCl_2$ with VSP in the presence of an excess of ammonium hydroxide gives a compound with the formula $[Cu_2(VSP-H)_2Cl_2]_n$. The deprotonation is confirmed by the effervescence resulting from the formation of HCl gas and the evolution of ethanoic acid during complex formation, and has been assessed quantitatively by both pH measurement and a spot-test technique, as well as detection of a characteristic odour[5,6].

The most significant change in the PVSP bands upon complexing (see *Table 2*) is the decrease in $\nu_{C=N}$. This shift to lower frequencies in the spectra of the complexes is likely to be due to involvement of the nitrogen atom of the C=N group in bond formation[5,6,11]. The lowering may be due to a reduction in the electron density in the azomethine link, whereas the ν_{OH} band almost disappears due to ionization of the OH group. The pyridine ring breathing mode is found at the same position in the spectra of the complexes, suggesting an absence of coordination through the nitrogen atom of the pyridine ring. This may be due to steric reasons since in this case an unstable four-membered ring should be formed. The $\nu_{C=N}$ stretching frequency is lowered in frequency by 23 cm^{-1} in the binuclear copper complex (when compared to the free ligand). Similar shifts of ν_{C-N} and ν_{C-O} to higher frequencies indicate the formation of a binuclear complex. The shift of the ν_{C-O} band by 25 cm^{-1} corresponds to bridging occurring through phenolic oxygens[2,12]. Other important characteristics of binuclear complex formation are the appearance of new bands of high intensity at around 1180, 1240–1250 and 1255–1260 cm^{-1}, plus the disappearance of bands near 1213–1220 cm^{-1} that were found in the mononuclear complexes[2]. Far-i.r. spectroscopic data of the complexes give an insight into the structure and bonding in the solid state. A medium to very strong Cu–Cl band at a frequency lower than 320 cm^{-1} in $[Cu(VSP-H)_2Cl_2]_n$ arises from the M–X vibration in a monomeric *trans*-structure[11].

The ν_{M-N} and ν_{M-O} assignments are in agreement with published literature data[1,5,6,9,12,13]. It is well known that metal–nitrogen stretching vibrations are often coupled with other normal modes of vibration of the same symmetry, especially ring vibrations, so the proposed assignments must be regarded as 'approximate' descriptions of the vibrations. The appearance of some new bands in the regions near 450 and 360 cm^{-1} are probably due to the formation of (M–O) and (M–N) bands, respectively.

The presence of the multiple covalent uranium–oxygen bond was established from the i.r. spectrum. The uranium complex which was synthesized in this work exhibits a very strong band at 710 cm^{-1}, characteristic of the asymmetric stretching frequency of the dioxouranium ion. The U–O bond distance was calculated by using the following equation[14]:

$$R_{U-O} = 1.08f^{-1/3} + 1.17 \quad (1)$$

where f is the force constant.

A bond distance of 1.74 Å was found which falls within the usual range for this group (1.60–1.92 Å).

Magnetochemical and spectroscopic studies

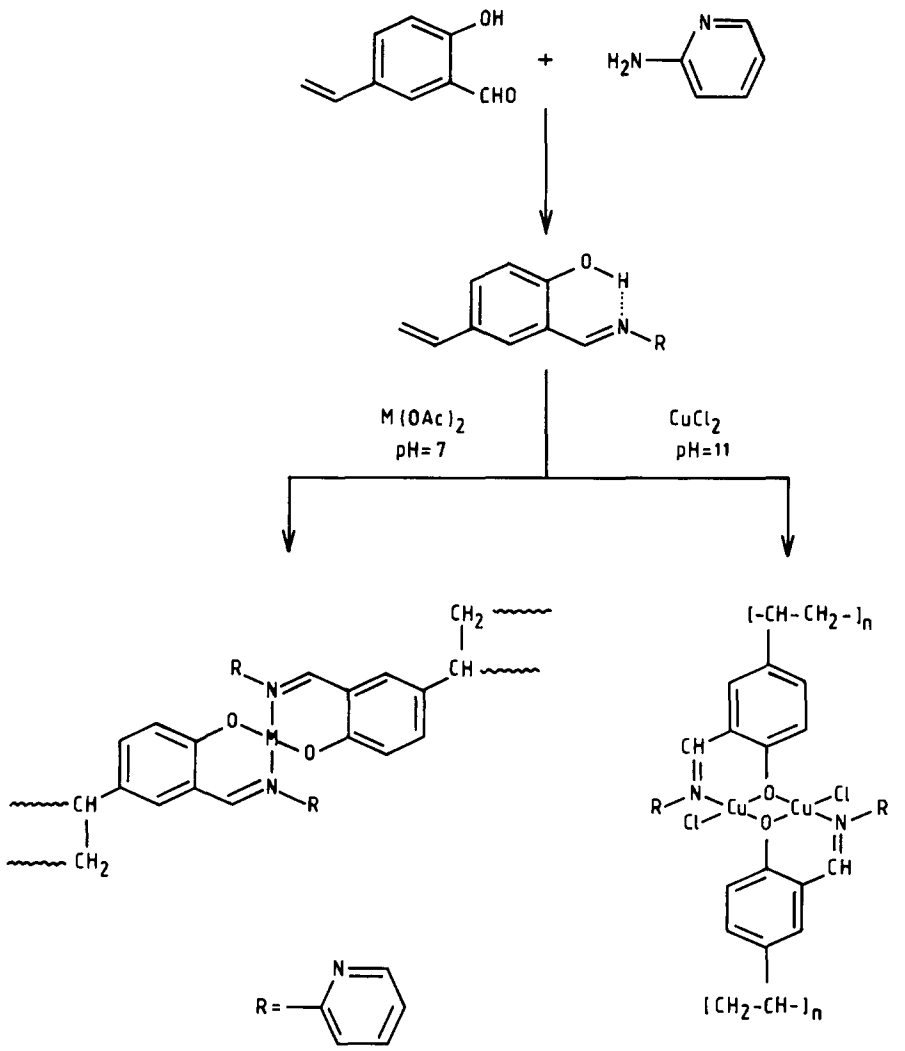
Tables 1 and *3* give the room-temperature magnetic moments and electronic spectroscopic data for all of the complexes, together with assignments and suggested geometries.

Electronic absorption bands for mononuclear copper(II) complexes were observed in the low-energy region. The lowest energy band at 14 685 cm^{-1} is assigned to a $^2E_1 \rightarrow {}^2E_2$ (d–d) transition and this occurs in the range found for a square planar type of geometry. The spectrum is consistent with the data reported for bis(1-butylsalicylidenaminato) copper(II) which has a distorted tetrahedral symmetry[15]. The magnetic moment

Table 3 Electronic spectroscopy bands, assignments and suggested geometries for the complexes of PVSP

Compound[a]	Band position (cm^{-1})	Assignment	Geometry	Ref.
VSP–$CuCl_2$	17 350	$^2T_{2g} \rightarrow {}^2E_g$	Tetrahedral	15
	20 980	Charge transfer		
VSP–CuX_2	14 680	$^2E_1 \rightarrow {}^2E_2$	Square planar	16
VSP–CoX_2[b]	8 197	$^4A_2 \rightarrow {}^4T_1(F)$	Tetrahedral	17
	16 672	$^4A_2 \rightarrow {}^4T_1(P)$		
	19 985	Charge transfer		
VSP–NiX_2	16 700	$^1A_{1g} \rightarrow {}^1A_{2g}$	Square planar	16
	21 630	$^1A_{1g} \rightarrow {}^1B_{1g}$		
VSP–PdX_2	23 100	$^1A_{1g} \rightarrow {}^1B_{1g}$	Square planar	18
VSP–UO_2X_2	17 360			
	22 630[c]			

[a] X is acetate ion
[b] $D_q = 485\ cm^{-1}$, $B = 692\ cm^{-1}$, $\beta = 0.71$
[c] Similar to the O–U–O symmetric stretching frequency for the first excited state



Scheme 1

of this complex is 1.89 μ_B which falls in the borderline region between square planar and tetrahedral symmetry[16]. The magnetic moment per copper(II) ion in the binuclear complex is 1.59 μ_B. In general, a decrease in the magnetic moment below the spin-only value (1.73 μ_B) was attributed to molecular association taking place to form bi- or polynuclear molecules. The low effective magnetic moment is attributed to antiferromagnetic superexchange interactions between two copper(II) ions through the phenolic oxygen bridge[2]. The electronic absorption bands at 17 350 and 20 980 cm^{-1} are indicative of a change in symmetry and a further distortion towards the tetrahedral conformation, when compared to that observed for the mononuclear copper(II) complex. Both mono- and binuclear copper(II) complexes must necessarily take the form of *trans-* structures, since a *cis-* structure will involve steric repulsion. The mononuclear and binuclear complexes may be represented as shown in *Scheme 1*.

The spectrum of $[Co(VSP–H)_2]_n$ displays two bands at 8197 and 16 672 cm^{-1}. These are assigned, respectively, as the $^4A_2 \rightarrow {}^4T_1(F)(\nu_2)$ and $^4A_2 \rightarrow {}^4T_1(P)(\nu_3)$ transitions of tetrahedral cobalt(II). The D_q, B and β values are calculated by the equations used for the d^7 system[17] and are listed in *Table 3*. The values agree fairly well with those previously reported for tetrahedral Co(II) complexes. A considerable reduction in the B value of the free ion on complex formation indicates the covalent character of the ligand-to-metal bond[5–7]. Distortion from a regular tetrahedral symmetry would be expected to be most noticeable in the $^4A_2 \rightarrow {}^4T_2(\nu_1)$ transition, but this latter is rarely observed and is derived theoretically. Furthermore, a charge-transfer transition is observed in the 19 985 cm^{-1} region which may be due to L→Co.

$[Ni(VSP–H)_2]_n$ exhibits a 16 700 cm^{-1} ($^1A_{1g} \rightarrow {}^1A_{2g}$) and a 21 630 cm^{-1} ($^1A_{1g} \rightarrow {}^1B_{1g}$) transition. The diamagnetic nature of this complex supports a square planar geometry[16]. Similarly, the diamagnetic nature of the palladium(II) complex also indicates square planar geometry, as would be expected for a d^8 metal ion. Furthermore, the electronic spectrum shows a band at 23 100 cm^{-1}, which is due to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition in a planar configuration[18].

The dioxouranium(VI) compound, with an equatorial coordination number of four, absorbs below 20 000 cm^{-1}; compounds with more than four equatorial groups do not show any absorption in this region. The $[UO_2(VSP–H)]_n$ complex shows two bands in its spectrum, the first at 22 630 cm^{-1} which can be definitely assigned to the $^1\varepsilon_g^+ \rightarrow {}^3\pi_u$ transition of dioxouranium(IV), and the second at 17 360 cm^{-1}, indicating an equatorial coordination number of four.

Spectroscopic studies of the homopolymer in solution

The electronic absorption spectrum of the homopolymer synthesized in this work was recorded in different organic

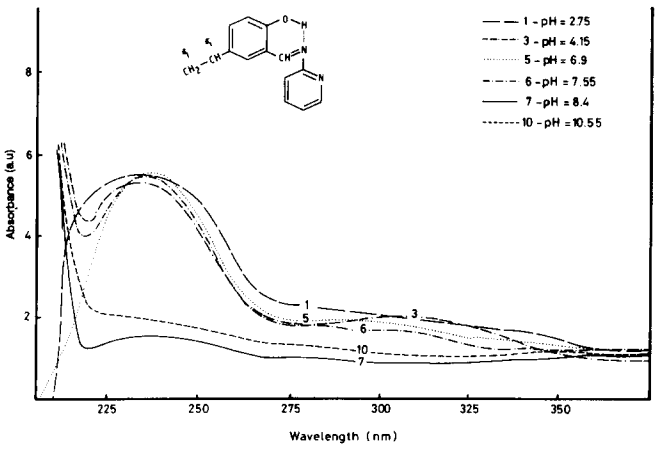


Figure 1 Absorption spectra of the PVSP homopolymer in buffer solutions (2×10^{-5} M) recorded at different pH values (system contains 50 vol% dioxane)

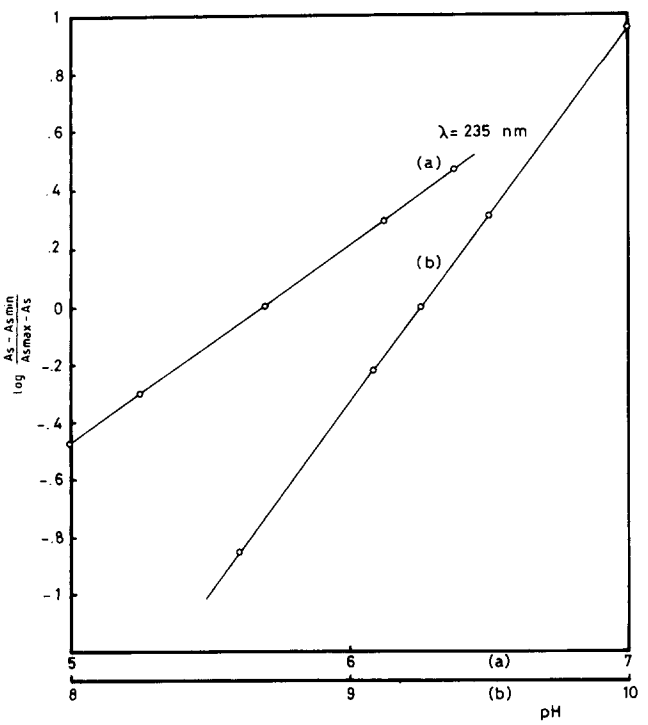


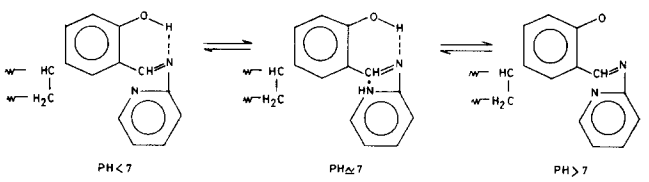
Figure 2 Variation of the absorbance of solutions of PVSP homopolymer with pH

solvents of varying polarities, and also in various buffer solutions with different pH values. Spectroscopic studies concerning the presence of certain metal ions under various conditions, as well as potentiometric titration of related systems, have been discussed elsewhere[8].

The u.v. spectra of the PVSP homopolymer in various organic solvents mainly display three bands, namely in the ranges 50 000–38 461 (A), 36 363–30 769 (B) and 33 333–27 777 (C) cm^{-1}, plus a broad shoulder (D) on the long-wavelength side of band (C), at 29 411–25 000 cm^{-1}. The three bands (A), (B) and (C) can be assigned to the π–π^* transition within the aromatic ring system and to locally excited transitions in the azomethine group, while the broad shoulder may be assigned to an intramolecular charge-transfer process.

The red shift of the bands (A), (B) and (C) with increased solvent polarity is of low magnitude when compared to that of band (D). The red shift in (D) is in agreement with the observations of Bayliss and Macram[19] and Schubert and Robins[20] who proposed that the polar solvent molecules of the excited state more than that from the ground state. The higher shifts in solvents such as ethanol and DMF can be ascribed to the ability of these solvents to act as proton donors or acceptors, in addition to their ability to act as n-electron donors towards the solute molecules. In the case of acetone or DMF the solvent molecules can behave as proton acceptors or electron donors[21]. Spectra of the PVSP homopolymer in buffer solutions containing 50 vol% of dioxane, recorded at different pH values, are shown in *Figure 1*.

In order to calculate the dissociation constant of PVSP spectrophotometrically, the absorbance is plotted against the pH of the solution (*Figure 2*). Accordingly, we can suggest the existence of the following equilibria:



The acid dissociation constant of the homopolymer was determined by applying the Colleter method[22], as modified for acid–base equilibria[23], as well as by the corrected limiting absorbance and isosbestic point[24] methods, by making use of the variation of the absorbance (As) with pH. The mean values obtained are 5.70 (pK_1) and 9.10 (pK_2), and 5.70 (pK_1) and 9.25 (pK_2), from the Colleter and the modified limiting absorbance methods, respectively. The identical pK_1 values of 5.70 could be attributed to the protonation constant of the pyridine nitrogen atom at pH < 7, while the pK_2 values of 9.10 and 9.25 were assigned to deprotonation of the phenolic group. This conclusion was reached by comparison of these results with those obtained for similar compounds[22–24].

A plot of $\log[(As - As_{min})/(As_{max} - As)]$ against pH would give a straight line of unit slope, and the intercept with the pH axis corresponds to the pK value. Although As, As_{max} and As_{min} are dependent on the wavelength that is chosen, the ratio $(As - As_{min})/(As_{max} - As)$ is independent of the wavelength, and therefore logarithmic plots of the latter against pH, measured for different wavelengths and different initial concentrations, should all fall on the same straight line. It can be seen that values of the dissociation constant obtained by the different methods are close to each other.

REFERENCES

1 El-Dissouky, A. and El-Sonbati, A. Z. *Polyhedron* 1990, **9**, 2443
2 El-Sonbati, A. Z. *Synth. React. Inorg. Metal-Org. Chem.* 1991, **21**, 203
3 Diab, M. A. and El-Sonbati, A. Z. *Polym. Degrad. Stabil.* 1990, **29**, 271
4 Grant, D. M. and Grassie, N. *J. Polym. Sci.* 1960, **42**, 587
5 El-Sonbati, A. Z. *Transition Met. Chem. (Weinheim, Ger.)* 1991, **16**, 45
6 El-Sonbati, A. Z. *Transition Met. Chem. (Weinheim, Ger.)* 1992, **17**, 19
7 El-Sonbati, A. Z. *Synth. React. Inorg. Metal-Org. Chem.* 1991, **21**, 977
8 El-Sonbati, A. Z., El-Bindary, A. A., Diab, M. A., El-Ela, M. A.

and Mazrouh, S. A. *Synth. React. Inorg. Metal-Org. Chem.* 1993, **23**, 875
9 El-Sonbati, A. Z., El-Bindary, A. A. and Mabrouk, E. M. *Transition Met. Chem. (Weinheim, Ger.)* 1992, **17**, 66
10 Diab, M. A., El-Sonbati, A. Z., El-Sanabari, A. A. and Taha, F. I. *Polym. Degrad. Stabil.* 1989, **24**, 51
11 El-Sonbati, A. Z., El-Bindary, A. A., Diab, M. A., El-Ela, M. A. and Mazrouh, S. A. *Monatsh. Chem.* in press
12 El-Sonbati, A. Z. and Hefni, M. A. *Monatsh. Chem.* 1993, 124, 419
13 El-Sonbati, A. Z., Diab, M. A., Kotb, M. F. and Killa, H. M. *Bull. Soc. Chim. Fr.* 1991, **128**, 623
14 El-Sonbati, A. Z. *Synth. React. Inorg. Metal-Org. Chem.* 1991, **21**, 1469
15 El-Shazly, M. F., El-Dissouky, A., Salem, T. M. and Osman, M. M. *Inorg. Chim. Acta* 1980, **40**, 1
16 Ray, P. and Sen, D. N. *J. Indian Chem. Soc.* 1948, **25**, 473
17 El-Sonbati, A. Z., Hassanien, A. A. and Hefni, M. A. *Spectrosc. Lett.* 1993, **12**, 1311
18 El-Sonbati, A. Z., Mabrouk, E. M. and Megahed, H. E. *Transition Met. Chem. (Weinheim, Ger.)* 1991, **16**, 280
19 Bayliss, N. S. and Macram, M. *Phys. Chem.* 1954, **58**, 1002
20 Schubert, W. M. and Robins, J. L. *J. Am. Chem. Soc.* 1960, **82**, 1453
21 Foster, R. 'Donor Acceptor Complexes', Academic, London, 1969
22 Colleter, J. C. *Am. Chem.* 1960, **5**, 415
23 Issa, R. M. *J. Chem. U.A.R.* 1971, **14**, 113
24 Issa, R. M., Ghoniem, M. M. and Harfoush, A. A. *Z. Phys. Chem. (Leipzig)* 1975, 94