

# FTIR study of self-protonation and gel formation in pyridinic solutions of poly(4-vinylpyridine)

Mark Rozenberg,\* Evgenya Vaganova and Shlomo Yitzchaik\*

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel. E-mail: markroz@chem.ch.huji.ac.il (M. Rozenberg), sy@cc.huji.ac.il (S. Yitzchaik)

Received (in Montpellier, France) 25th August 1999, Accepted 1st February 2000

**An FTIR study reveals the complex zwitterion ( $R_2C^- - Py^+ - H$ ) in a polymeric chain of poly(4-vinylpyridine), which results from self-protonation of the latter in a pyridine solution. Presumably this complex ion, together with the observed strongly hydrogen-bonded network, is responsible for the formation of a gel with unique tunable emission properties.**

We recently showed that a pyridinic solution of poly(4-vinylpyridine) (P4VP) turns spontaneously into a photoactive gel with unique tunable emission properties, which can be tuned to glow blue, red or green, depending on the pumping wavelength.<sup>1</sup> In this contribution a study of the gelation process is performed by FTIR spectroscopy in order to elucidate the molecular building blocks of these “smart gels”. The formation of supramolecular ordering in these smart gels by strong hydrogen bonds is also shown.

The FTIR spectra of gel samples with a molar ratio varying from 1 : 4 to 1 : 1 between the P4VP repeating unit and pyridine (Py) were studied. Samples of commercial P4VP [ $M_w = 50\,000$ ; Polysciences, Inc.), initially containing approximately 6% water, dried in vacuum at 140 °C or by heating at 220–240 °C under nitrogen atmosphere up to melting, were studied. There was no difference in the subsequent sample behavior between the two drying methods and the latter was used in the following experiments.

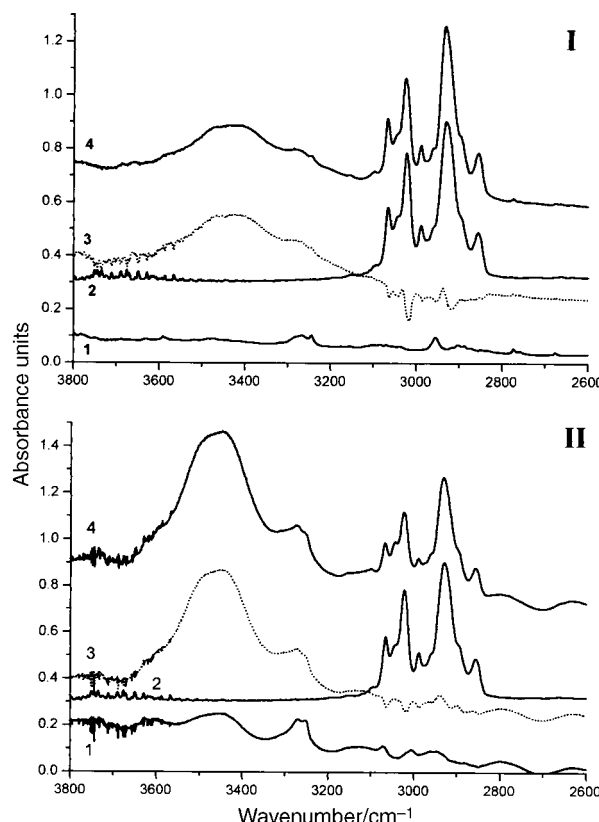
Py- $d_5$  and Py (99.8%, anhydrous), dimethyl sulfoxide (DMSO- $d_6$ ), dioxane and absolute ethyl alcohol were commercial samples (Aldrich). Prior to gel preparation Py and Py- $d_5$  were degassed; all solvents were dried and stored over molecular sieves. The water content in solvents was monitored by IR spectroscopy and did not exceed 0.03 M or 0.04 wt%; in the pure P4VP after drying and in gel samples the water content, which was determined by the Fisher method in methanol solution, did not exceed 0.01 wt%. Deuterium exchange in dried gel films was carried out with  $D_2O$  vapors in a  $N_2$  flow at 60–80 °C.

IR spectra were recorded in 0.01–0.03 mm  $CaF_2$  cells on a Bruker 113v FTIR spectrometer with a nominal resolution of 1  $cm^{-1}$  and processed by the Bruker OPUS program. For quantitative comparison the spectra of initial P4VP film and solutions (gel samples) were normalized with the bands at 1220 and 1068  $cm^{-1}$ , which are assigned to proton deformation modes of the 4-substituted pyridine ring<sup>2</sup> and are not affected by dissolution.

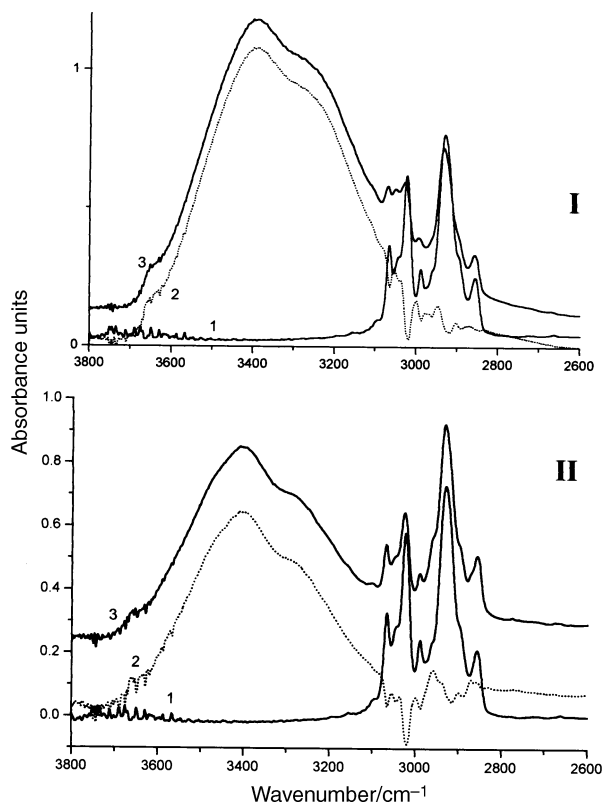
In the spectrum of a pyridinic solution of P4VP [Fig. 1(I), trace 4], a new intense and wide (300  $cm^{-1}$ ) asymmetric absorption band appears at 3400  $cm^{-1}$  when compared with the spectra of pure polymer (trace 2) and solvent (trace 1). A similarly wide (250  $cm^{-1}$ ) band at somewhat higher frequency (3450  $cm^{-1}$ ) also appears in the spectrum of solutions of P4VP in DMSO [see Fig. 1(II), trace 4]. A similar band is also observed in the spectrum of pure polymer precipitated

from ethanol [Fig. 2(I), trace 3]. In the latter, besides the presence of this new band and a noticeable intensity change in the CH absorption bands (see below), no other changes were noticed in the range of the skeletal vibration modes (below 2000  $cm^{-1}$ ). A similar band with a more complex structure is also present in the spectrum of P4VP swollen in dioxane. The spectrum of an accurately (without overheating) prepared film of pure P4VP, as well as the spectra of the solvents, do not reveal any trace of the band near 3400  $cm^{-1}$  [Fig. 1(I), trace 2; see also ref. 3].

This band is also present in the spectrum of a film prepared by drying the Py out of the gel. When the film of such a gel is treated with  $D_2O$  the intensity of the band at 3400  $cm^{-1}$  decreases and a new band near 2500  $cm^{-1}$  (not shown) appears with the “harmonic” isotopic frequency ratio  $\nu/\nu' = 1.37$ . Such behavior following D-exchange confirms the assignment of the band near 3400  $cm^{-1}$  to a proton vibration.



**Fig. 1** IR spectra of melted P4VP samples in pyridine- $d_5$  (I) and in DMSO- $d_6$  (II) solutions. Trace 1: neat solvent, trace 2: P4VP film prepared by melting, trace 3: differential spectrum (trace 4 – trace 2) and trace 4: after dissolution (50 wt% P4VP : Py).



**Fig. 2** (I) IR spectra of pure P4VP samples. Trace 1: film prepared by melting, trace 2: differential spectrum (trace 3 – trace 1) and trace 3: reprecipitated from ethanol. (II) IR spectra of gel samples prepared from an unmelted P4VP sample containing 3% water. Trace 1: film prepared by melting, trace 2: differential spectrum (trace 3 – trace 1) and trace 3: after dissolution (50 wt% P4VP : Py).

The band at 3400 cm<sup>-1</sup> for the Py solution and gel (and also in other solvents) may be assigned to the stretching vibration of the N<sup>+</sup>H bond of the pyridinium ion (Py<sup>+</sup>H) bound with solvent by quite weak (4–8 kJ mol<sup>-1</sup>) H bonds in pyridinic media. We assigned this band to the pyridinium proton, since the band of a neutral NH group, H-bound with Py (and also with DMSO), would be positioned at approximately 3150 cm<sup>-1</sup>. The low-frequency shoulder at 3300 cm<sup>-1</sup> can be, presumably, assigned to an overtone of the N–H deformation mode at 1600 cm<sup>-1</sup>, intensified by Fermi resonance (see, for example, ref. 4). The latter is seen in all solution spectra as a weak band, which also disappears with D-exchange. The band at 3400 cm<sup>-1</sup> cannot originate from water contamination of melted samples because the estimated small quantity of water, if it is present, cannot account for more than 10% of the observed absorption band. The molar intensity of the band at 3400 cm<sup>-1</sup> is approximately two times larger than estimated [(1.2 ± 0.8) × 10<sup>-4</sup> cm mmol<sup>-1</sup>] in the literature<sup>5</sup> for free Py<sup>+</sup>H ions and averages 2.5 × 10<sup>-4</sup> cm mmol<sup>-1</sup> per Py<sup>+</sup>H ion.

The Py<sup>+</sup>H ion is formed at the pyridine side-group of the polymer. Firstly, the 3400 cm<sup>-1</sup> band intensity increases with the polymer concentration in pyridinic solution. Secondly, this band is also observed in the dried gel film, which does not contain free pyridine, and also in the polymer after treatment with ethanol and elimination of the latter. The proton transfer reaction is irreversible and it results in some sort of a similar salt compound.

The initial proton source is certainly the polymeric methyne groups. In Fig. 1, traces 4, and Fig. 2, traces 3, the changes in the range of ν(CH) vibrations are obvious. The band at 3026 cm<sup>-1</sup> in the solution (and gel) spectra is weaker relative to the ν(CH<sub>2</sub>) band at 2932 cm<sup>-1</sup> in comparison with the spectra of pure polymer [Fig. 1(I) and (II), traces 4 and 2; Fig. 2(I) and

(II), traces 3 and 1]. The negative uncompensated narrow bands at 3064.0, 3017.7 and 2987.5 cm<sup>-1</sup> are seen in all difference spectra of solutions in Py-d<sub>5</sub> and DMSO-d<sub>6</sub> and pure polymer. The most intense negative band at 3017.7 cm<sup>-1</sup> definitely belongs to the acidic proton of the polymeric CH groups, whose amount decreases on dissolution. The small positive and wide peaks at 2960 and 2860 cm<sup>-1</sup> in the differential spectrum can be assigned to acidic CH groups, which are H-bound with pyridine. It should be noted that the negative peak at 3017 cm<sup>-1</sup> is present in the spectra of polymer samples reprecipitated from ethanol—a proton donor—after solvent elimination. This band is also present for a gel sample containing approximately 3% water [Fig. 2(II), trace 2]. Thus, the presence of stronger proton donors does not inhibit deprotonation of the P4VP methyne proton.

If our suggestion holds true and the decrease of the CH and the amount of the N<sup>+</sup>H groups are interconnected, then the intensity of the CH band can be estimated from the ratio of (S<sub>N+H</sub>/A<sub>N+H</sub>)/(S<sub>CH</sub>/A<sub>CH</sub>) = 1. Here S<sub>N+H</sub> and S<sub>CH</sub> are the areas under the positive (at 3400 cm<sup>-1</sup>) and negative (3064.0–2987.5 cm<sup>-1</sup>) absorbency areas, and A<sub>N+H</sub> and A<sub>CH</sub> are the molar integral absorption coefficients of the N<sup>+</sup>H band and CH bands, respectively [estimated from Fig. 2(I), trace 3]. The magnitude of A<sub>CH</sub> is estimated to be 0.16 × 10<sup>4</sup> cm mmol<sup>-1</sup>, like the CH band of chloroform in benzene solution.<sup>6</sup> The accuracy of this estimate is not high, but it shows that the amounts of both groups are indeed of the same order of magnitude. Assuming that the acidity of these CH groups is equal to that in chloroform,<sup>7</sup> the energy of the H bond can be estimated. It follows from the red shift, which is approximately 60 cm<sup>-1</sup>, that the H bond energy is 6–8 kJ mol<sup>-1</sup>. A possible reason for this unusual acidity of the tertiary proton in P4VP can be ascribed to a “cooperative” effect of the pyridine side groups on the hydrocarbon chain. Detailed consideration of differential spectra shows that not only bands at frequencies higher than 3000 cm<sup>-1</sup> are influenced, but also the bands of the CH<sub>2</sub> groups at 2900 cm<sup>-1</sup>.

The position of the N<sup>+</sup>H band of pyridinium salts in solution strongly depends on the type of counter anion.<sup>5</sup> The peak frequency increases from 2300 cm<sup>-1</sup> in Py<sup>+</sup>HCl<sup>-</sup> to 3200 cm<sup>-1</sup> in Py<sup>+</sup>HClO<sub>4</sub><sup>-</sup>, that is it depends on anion basicity, which, in turn, is connected with the ionic radius. The higher frequency (3400 cm<sup>-1</sup>) in our case shows that Py<sup>+</sup>H is bound with a weaker basic center that is effectively bigger than the ClO<sub>4</sub><sup>-</sup> anion. The carbanions that are produced after proton elimination can possibly account for these “big size” (macromolecular) low basicity anions and also for the weak H bond formation of Py<sup>+</sup>H with a quite high proton vibration frequency. The observed high intensity of the band at 3400 cm<sup>-1</sup> results from the high molar concentration of pyridinic side chain groups.

The presence of analogous bands in solutions of P4VP in DMSO and in dioxane also confirms the idea of self-protonation of P4VP and formation of PyN<sup>+</sup>H at the Py side-group of the polymer. In this case the higher ν(N<sup>+</sup>H) peak position can be explained by the weaker (CH<sub>3</sub>)<sub>2</sub>SO···H<sup>+</sup>PyR H bond, because DMSO (and dioxane) are weaker bases than Py. It should be noted that in the spectra of solutions of P4VP in pyridine the new narrow and weak band at 1588 cm<sup>-1</sup> appears with increasing polymer concentration. Presumably this band can be related to the (C–C) aromatic ring vibration of this complex ion. In the gel film spectrum a new band at 1666 cm<sup>-1</sup> also appears. The closest analog of the latter is the “immonium” band of the [–C=N<sup>+</sup>–(H)R] group<sup>8</sup> but its origin in our case remains unclear. The difference between the solution spectra of humid and anhydrous P4VP samples is only quantitative—it appears as if a band due to water that is H-bound with solvent is superimposed at 3400 cm<sup>-1</sup>, increasing the observed absorption band [Fig. 2(II)].

It should be noted that the IR spectra of the gel (and its optical properties) are sensitive to the water content. In the spectrum of gel that contains approximately 3% water, after some time (16 h) the intensity of the  $3400\text{ cm}^{-1}$  band noticeably decreases and a very wide absorbency centered below  $1700\text{ cm}^{-1}$  appears in the spectra [Fig. 3(I) and (II)]. The decrease of the  $\text{Py}^+\text{H}$  band in the gelation process and the increase of the continuous absorbency band below  $1700\text{ cm}^{-1}$  possibly suggests the formation of symmetrical H bonds ( $\text{Py}\cdots\text{H}\cdots\text{Py}$ )<sup>+</sup> from two  $\text{Py}^+\text{H}$  groups—or, more likely—between two chains. Water (or another proton donor), which can be present in pre-cleaned polymer and is absent in the polymer sample after melting, can catalyse this process as does ethanol. Such very intense bands for  $\text{Py}^+\text{H}$  ion-containing systems have been observed in the IR spectra of crystals and solutions<sup>6,10,11</sup> and these data can be a reliable base for the interpretation of our observations. These symmetrical H bonds are quite strong ( $50\text{ kJ mol}^{-1}$ )<sup>9</sup> and can form an H bonding network during gel formation.

Several steps can represent the process of optically active media formation. The formation of an H bond ( $\text{R}-\text{CH}\cdots\text{Py}$ ) to pyridine ( $\text{pK}_a = 5.22$ ) with an acidic CH proton is followed by proton transfer to the pyridine. The latter transfers the proton to the Py side-group ( $\text{pK}_a = 6.04$  for 4-

isopropylpyridine,<sup>10</sup> which can be taken as an analog of P4VP) repeating unit, but some of them remain bound to the carbanion by weak ( $4\text{--}6\text{ kJ mol}^{-1}$ ) H bonds. The same H bonds are also formed between  $\text{Py}^+\text{H}$  radicals and carbanions of neighboring chains:  $\text{C}^-\text{PyH}^+\cdots\text{C}^-\text{PyH}^+$ . Our results stress the importance of taking into account H bond interactions in optically active and conducting polymers, in line with previous, although not numerous, data.<sup>11,12</sup>

Other authors<sup>13</sup> have mentioned protonation of the pyridine ring of P4VP and, as shown in published spectra, had observed the band at  $3400\text{ cm}^{-1}$  in a polymeric blend of P4VP with a polymeric sulfonic acid. But, possibly because of the strong acid band present in this region, they did not mention this observation or discuss it. The  $3400\text{ cm}^{-1}$  band was also recently<sup>14</sup> observed in spectra of tetrazole mixtures with a very strong base, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene. The assignment of this band to the free protonated  $\text{N}^+\text{H}$  group of this base supports our suggestion about the presence of a similar group in P4VP gels or solutions.†

## Acknowledgements

M. R. and E. V. gratefully acknowledge financial support from the Israel Ministry for Immigrant Absorption, S. Y. thanks the German Israeli Science Foundation (GIF no. 355.032.05/95).

## Notes and references

† Note added at proof: the detailed mechanism for stabilization of the solid (after dissolution) ionic form of P4VP remains unknown.

- 1 E. Vaganova and S. Yitzchaik, *Acta Polym.*, 1998, **49**, 632; E. Vaganova, M. Rozenberg and S. Yitzchaik, *Chem. Mater.*, in press.
- 2 A. R. Katritzky, *Q. Rev. Chem. Soc.*, 1959, **13**, 353.
- 3 J. L. Velada, L. C. Cesteros and I. Katime, *Appl. Spectrosc.*, 1996, **50**, 893.
- 4 G. A. Kurkchi and A. V. Iogansen, *Russ. J. Phys. Chem.*, 1991, **65**, 1240.
- 5 A. V. Iogansen, S. A. Kiselev, B. V. Rassadin and A. A. Samoilenko, *J. Struct. Chem. (USSR)*, 1976, **17**, 546.
- 6 A. V. Iogansen, *Spectrochim. Acta, Part A*, 1999, **55**, 1585.
- 7 A. V. Iogansen, *Teor. Eksp. Khim. (SSSR)*, 1971, **7**, 302 (Russ).
- 8 A. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley, New York, 1972, Table 101.
- 9 S. E. Odinokov, A. A. Mashkovsky, V. P. Glazunov, A. V. Iogansen and B. V. Rassadin, *Spectrochim. Acta, Part A*, 1976, **32**, 1355.
- 10 A. Rabold, R. Bauer and G. Zundel, *J. Phys. Chem.*, 1995, **99**, 1889.
- 11 P. Colomban, A. Gruger, A. Novak and A. Regis, *J. Mol. Struct.*, 1994, **317**, 261.
- 12 A. Gruger, A. Novak, A. Regis and P. Colomban, *J. Mol. Struct.*, 1994, **328**, 153.
- 13 M. B. Huglin and J. M. Rego, *Polymer*, 1990, **31**, 1269.
- 14 B. Brzezinski, G. Wojciechowski, G. Zundel, L. Sobczyk and E. Grech, *J. Mol. Struct.*, 1999, **508**, 175.

Letter a906937b

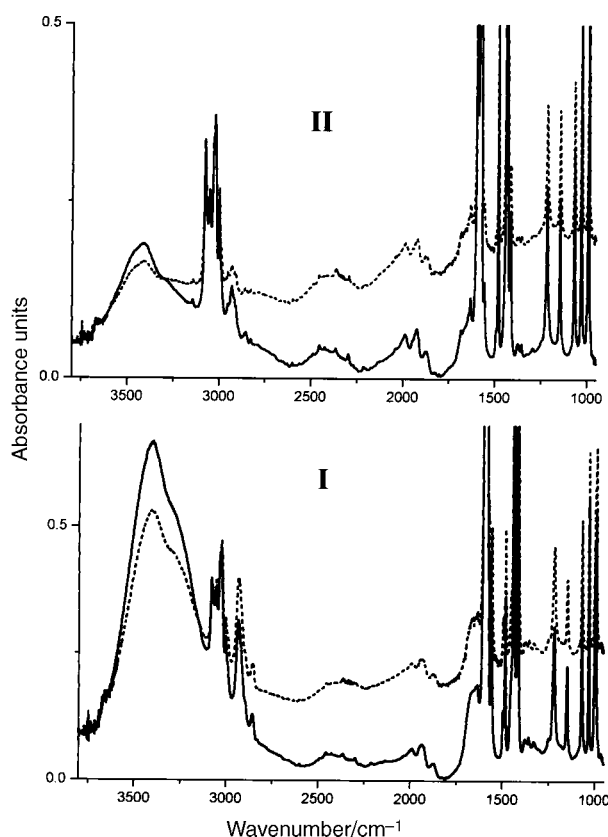


Fig. 3 IR spectra of pyridinic solutions of unmelted P4VP samples. (I) 50 wt% Py and (II) 10 wt% Py, fresh solution (solid line) and after approximately 16 h (dotted line).