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Acidity of the Methyne Group of Poly(4-vinylpyridine) leads to Side-chain Protonation in Pyridine

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Poly(4-vinyl pyridine) swollen in pyridine displays changes in electrical conductivity in response to white light and to low level thermal perturbation; protonation of the side-chain nitrogen is believed to play a role. Here we present spectroscopic evidence that the proton donor is the methyne group CH on the polymer chain.

Poly(4-vinylpyridine) (P4VP) is one of the most commonly used polymers in the construction of layered films as well as serving as a matrix for the embedding of semiconductor nanoparticles.[1,2] Because of the lone pair of sp^2 electrons, P4VP demonstrates interesting photochemical properties leading to various applications such as coatings that respond to changes in pH.[3] When P4VP is dissolved in dry liquid pyridine and allowed to gel, unique opto- and thermo-electronic behavior is observed. These properties have been studied extensively during the last few years, both experimentally[4-6] and using computational methods.[7] Previously it was suggested that the unique optical properties of the P4VP gel are related to the transfer of a methyne proton to a side chain pyridine nitrogen with the formation of a pyridinium ion NH$^+$.[8] This suggestion was based on a comparison of the FTIR spectra of the initial P4VP film and the P4VP/pyridine gel in the frequency range 2800-3200 cm^{-1} where absorption bands due to the stretching modes of CH and CH$_2$ groups can be observed. Because the molar intensity of the CH stretching vibration is very small, the changes in this spectral range were clear but relatively subtle. The loss of intensity in the methyne bands at 3010-3030 cm^{-1} in the gel spectrum was attributed to loss of methyne protons in the P4VP structure. A new, very strong infrared band at 3400 cm^{-1} in the gel was assigned to the NH$^+$ stretching vibration of the pyridinium ion. Proton transfer under UV irradiation to form a pyridinium ion was also observed by NMR spectroscopy.[6] Modeling suggested that the mobile pyridine solvent molecule acts as a proton transfer vehicle.[6]

Here we present additional evidence for the acidity of the methyne group of P4VP. It is well known that proton donors in hydrogen bond complex formation such as OH, NH, and SH groups, readily undergo hydrogen-deuterium exchange upon contact with heavy water.[9,10] If the earlier suggestion concerning the acidity[8] is correct, it would be expected that the methyne CH group should also readily undergo deuterium exchange. By contrast, deuterium exchange of pyridine ring protons requires a catalyst and elevated (160^0C) temperature.[11] Methylene group protons also cannot be exchanged at temperatures below 100^0C without a catalyst.[12,13] Indeed we find that the FTIR spectrum of poly(4-vinylpyridine) treated with heavy water , heated and then dissolved in dry pyridine reveals a broad and intense absorption band centered at a frequency *ca.*2500 cm^{-1}, that is consistent with the ND$^+$ stretching vibration. A similar absorption band is also observed at 3400 cm^{-1} and is attributed to the NH$^+$ stretching vibration resulting from incomplete exchange. We identify the ND$^+$ group as being formed by the self-deuteration of the polymer sidechain via liquid pyridine facilitated transfer of the methyne deuteron to the sidechain nitrogen.

P4VP and heavy water were purchased from Aldrich. Dry pyridine was purchased from Sigma-Aldrich (HPLC, ≥ 99.9%) The treatment of P4VP with liquid D$_2$O was performed in inert solvent (cyclohexane, Aldrich) according to the procedure described.[14] The special feature of this technique is that the heavy water is distilled with a recirculating inert, relatively low boiling point solvent-hydrocarbon or CCl$_4$ - in which water volatility is very high. A portion of ~ 3g of polymer was mixed with 50 ml of cyclohexane, heated to the boiling point of the solvent (81^0C) and then small quantities (1 ml) of D$_2$O were added. The heavy water was renewed for each portion of polymer. This procedure takes approximately one hour.

Powder samples, as-purchased and deuterated, were prepared as films for FTIR measurements by heating between two KBr plates at 130-140^0C during 10 min. For preparation of the gel samples, deuterated powder was first heated under nitrogen at 130 ^{o}C during 20min and then dissolved in dry liquid pyridine 1:1 molar ratio pyridine/P4VP side chains. After gelation during two hours under nitrogen, spectra were measured at room temperature using the Bruker Equinox 55 FTIR spectrometer at spectral resolution of 2 cm^{-1}.

The geometry optimized structure and natural bond orbital (NBO) charge distribution of the P4VP monomer, the P4VP monomer with protonated polymer side-chain and neighboring liquid pyridine molecule were calculated using the B3LYP hybrid density functional

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† Electronic Supplementary Information (ESI) available: (a) NBO charge distributions for singlet (^{1}A) and triplet (^{3}A) states of the polymer side chain and the cation (^{2}A$^+$) and anion (^{2}A$^-$) radical states; (b) Total energy without (E$_{tot}$) and with (E$_{tot}$(ZPE)) zero point energy corrections (in au) for singlet (^{1}A) and triplet (^{3}A) states of the polymer sidechain and the cation (^{2}A$^+$) and anion (^{2}A$^-$) radical states; (c) IR frequencies and intensities for the protonated side chain pyridine/free pyridine complex; See DOI: 10.1039/x0xx00000x

in conjunction with the Pople 6-311++G(d,p) basis set as implemented in the Gaussian-09 package.[15] It was necessary to calculate the charge distributions for singlet, triplet and two doublet states (anion and cation radicals) because the polymer side-chain in pyridinic solution can exist in different electronic states.[7] IR frequencies of the optimized protonated complex were calculated using the PBE1PBE hybrid density functional method[16] in combination with the Dunning correlation consistent polarized valence double ξ (cc-pVDZ) basis set.[17]

Figure 1 shows the FTIR spectra of polymer films prepared by heating the as-purchased P4VP powder (trace 1); P4VP powder following D_2O treatment (trace 2); and after dissolving the heated, deuterated polymer in dry pyridine, forming a gel (trace 3).

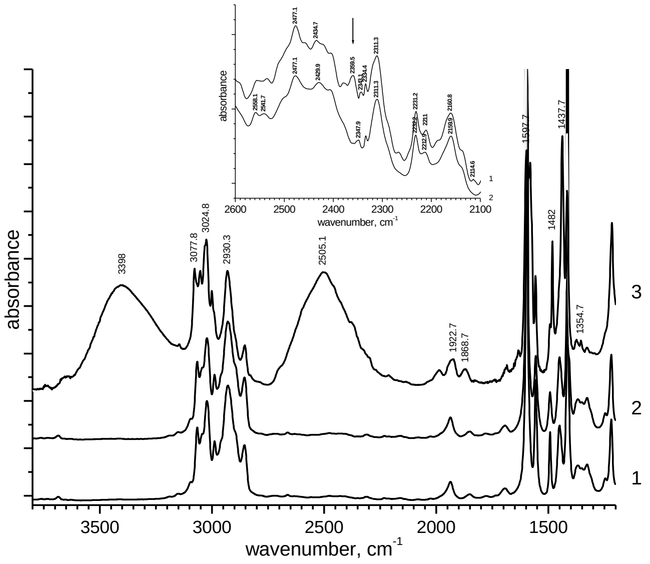

Figure 1. FTIR spectra of poly(4-vinylpyridine) films in the region 4000-400 cm^{-1}: 1- Film formed from the as- purchased powder; 2 – Film formed from the powder following D_2O treatment; 3 – Film formed following dissolution of the D_2O treated polymer in dry pyridine. Inset: FTIR spectra of P4VP films in the region of the CD stretching mode: 1- Film from the as-purchased powder; 2 – Film from powder following D_2O treatment. The arrow in the inset shows the new band assigned to the CD stretching vibration.

No obvious difference between traces 1 and 2, arising from the hydrogen-deuterium exchange of the polymer powder, can be observed in the range of stretching CH_2 modes near 2800-3100 cm^{-1} and in the range of skeletal polymer pyridine modes below 2000 cm^{-1}. However, the inset shows the enlarged FTIR spectra for both films in the range (2100-2600cm^{-1}), which includes the frequencies of CD stretching vibrations. There are several new, very weak, narrow bands between 2330-2360 cm^{-1} with isotopic frequency ratio *ca* 1.30 with respect to the stretching CH mode but these assignments are not certain. In general, the molar intensity of the stretching vibration of CH groups is very small: an estimate made on the basis of measurements of chloroform in benzene solution gives ~ 0.16x10^4 cm mmol^{-1}.[8] The integral molar intensity of the isotopic CD band is half that of CH band.[18] In the FTIR spectrum of the deuterated polymer gel (trace 3), a broad and intense band appears at 2500 cm^{-1} together with a similar band at 3400 cm^{-1}. The former is attributed to the ND^+ stretching vibration (see below) while the latter indicates the presence of NH^+ groups due to unexchanged hydrogen. The frequency isotopic ratio (1.36) is consistent with this assignment. The relatively large bandwidths of both bands are readily explained by the structural disorder of the polymeric side chains in the gel.[19] The degree of N->D exchange of the polymer, as determined by the intensity ratio of the NH^+ and ND^+ bands, is approximately 60-70%. This takes into account the fact that the molar intensity of the ND stretching vibration is only half that of the NH mode.[18] Back exchange can also be observed if the deuterated gel is left in air.

Figure 2A presents the results of NBO calculations for the singlet state of the P4VP monomer which show that there is less negative charge on the methyne carbon as compared to the methylene carbon. This is true for all electronic states as can be seen in the Table ESI† 1 of ESI†. In Figure 2B is shown the calculated infrared spectrum in the range 10-3500 cm^{-1} of the DFT optimized P4VP monomer following transfer of the methyne proton to the side chain nitrogen (details in ESI†). A neighboring liquid pyridine molecule, believed to function as the transport vehicle for the proton transfer, was included in the optimization (inset). The charge distributions confirm the higher methyne proton acidity relative to other protons in the P4VP structure. The dominant spectral feature is the very intense peak at 3382 cm^{-1} with calculated molar intensity *ca*. 2287 km mol^{-1}. It can be assigned to the NH stretching vibration (ESI †). Such a band was also observed for the stable 1-isomer of protonated pyridine ($C_5H_5NH^+$) produced upon electron bombardment during deposition of pyridine in a para-H_2 matrix at 3.2 K.[20]

In conclusion, we have shown that the acidity of the methyne groups can be identified as being an essential component in the process of protonation of the side chain nitrogens in a P4VP/pyridine gel. Details of the way in which this process contributes to the optical and thermal sensitivity of the gel remain to be clarified. Nevertheless, as elucidated here, the fact that the methyne group can act as a proton donor has important ramifications for other systems in which the poly (4-vinylpyridine) polymer plays a central role. Indeed, the polymer should be considered as being able to function not only as a base but also as an acid.

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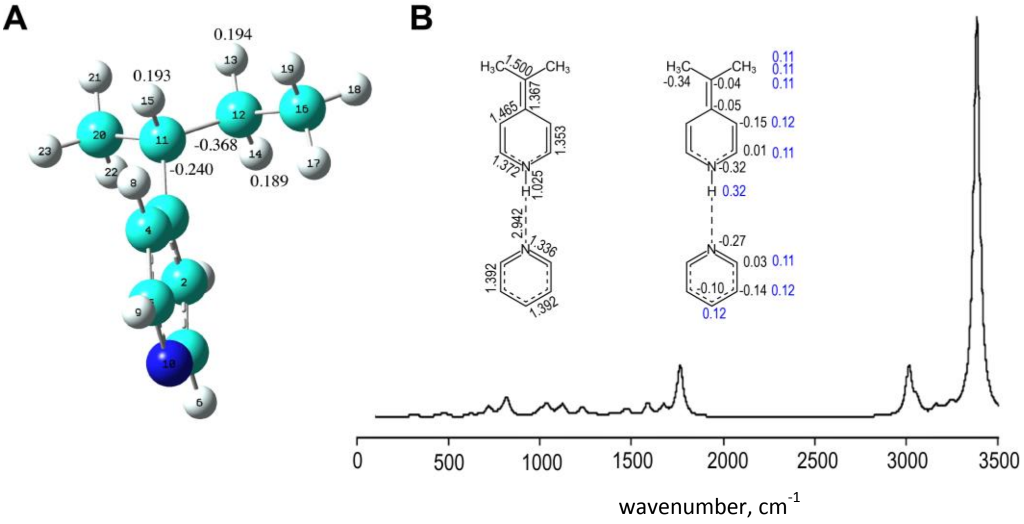

Figure 2 A. NBO charge distribution (in *electrons*) for atoms: C11, H 15 (methyne group) and C12, H13, H14 (methylene group) obtained with the B3LYP/6-311++G(d,p) geometry optimized poly(4-vinyl pyridine) side chain model in the singlet state. Color key: C-light blue; H-white; N-blue. B. Calculated FTIR spectrum of the protonated side chain pyridine / free pyridine complex. Insert: Structure (left scheme; bond lengths are in Angstroms) and NBO charge distribution (right scheme). Black font – charge on carbon; blue font – charge on hydrogen.

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Radiation sensitivity of poly(4-vinyl pyridine)/pyridine likely involves side-chain N-protonation. IR spectroscopy shows that the proton donor is the methyne CH.