

# Proton-Transfer Reactions of Poly(2-vinylpyridine) in the First Singlet Excited State

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**ABSTRACT:** The pH dependence of poly(2-vinylpyridine) (P2VP) emission in 50% alcohol/water and in aqueous solutions has been studied and compared with the emission of 2-ethylpyridine (EP) as a model compound. In acid-free solutions or at low acid concentrations, only an emission at 350 nm characteristic of solvents which form hydrogen bonds with pyridine is observed. Increasing the acid concentration up to a value that depends on the solvent causes a new emission at ca. 390 nm to be produced and is assigned to emission from a protonated form of the heterocycles. At higher acid concentrations, the 390-nm emission is quenched possibly by the formation of charge-transfer complexes or the counterion and the protonated form. The observation of only one of the above-described emissions with protonated and unprotonated rings in the ground state is interpreted as a proton-transfer reaction in the excited state. Such behavior is not observed for 2-ethylpyridine, and consequently, it is proposed to be a "polymer effect". No change is observed in the absorption spectra of the polymer and the monomer analogue by protonation, because it involves only the n levels, and the  $n, \pi^*$  absorption is hidden under the  $\pi, \pi^*$  band of larger extinction coefficient. However, the formation of charge-transfer complexes causes complete loss of all vibrational structure in the absorption spectra of P2VP.

## Introduction

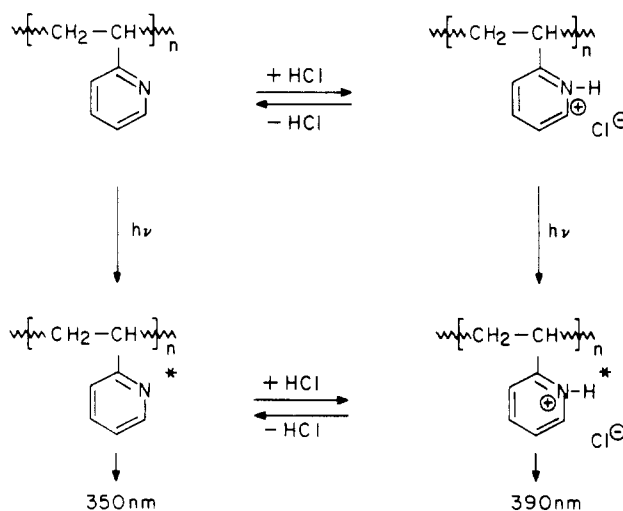
We have discovered that poly(2-vinylpyridine) (P2VP) displays a strong solvent dependence of its monomer fluorescence emission,<sup>1</sup> and also a significant pH dependence of its monomer fluorescence emission. In the ground state of P2VP,  $S_0$ , specific interactions of pyridine-solvent are not inhibited by steric factors of the chain skeleton, and as a result, the  $\pi$  cloud of the ring and the  $\pi-\pi^*$  transition are not significantly disturbed by solvent. However, the pyridine (P) heterocycles of P2VP are basic, and there is experimental evidence for ground-state protonation in acid solutions<sup>2-4</sup> as shown in Scheme I for P2VP.

The basic strength of the first excited singlet state,  $S_1^*$ , is in general different from  $S_0$ .<sup>5</sup> As a result, pH dependence and a dual emission occurs for many compounds, such as phenols, thiols, nitrogen and sulfur heterocycles, aromatic amines, carboxylic acids, aldehydes, and ketones. For example, a dual emission observed for 1-naphthylamine-4-sulfonate is attributed to a change in the  $pK_a$  of the aromatic molecule as a consequence of electronic excitation.<sup>6</sup> When a hydrogen-bonding chromophore absorbs a photon, the ground-state solvation equilibrium is no longer optimal and a reaction of protonation or deprotonation is required to reach the excited-state equilibrium. These excited-state reactions involving proton transfers are involved in many biological processes, such as the photoinduced visual process or the ATP synthesis in mitochondria and chloroplasts.<sup>7</sup> Excited-state proton transfers have been extensively studied in the gas phase and in solution of small molecules,<sup>8-13</sup> but have rarely been reported for polymer systems. We initiated investigations of the pH dependence of fluorescence of P2VP because we felt that it would be relevant to investigations of proton-transfer phenomena in polymer solutions, due to their special characteristics, i.e., high local concentration of chromophores with special entropy and free volume properties. The object of this work was to study the pH dependence of molecular electronic absorption and emission spectra of P2VP to determine the relevance of proton-transfer reactions of chromophores linked by a macromolecular chain.

## Experimental Section

P2VP was purchased from Polysciences Co. and was purified by three reprecipitations in two solvent-precipitant systems:

Scheme I  
Ground- and Excited-State Equilibria for the Poly(2-vinylpyridine) Acid-Base System<sup>a</sup>



<sup>a</sup> The emission at 350 nm is attributed to hydrogen-bonded excited heterocycles and the emission at 390 nm is attributed to protonated heterocycles. See text for discussion.

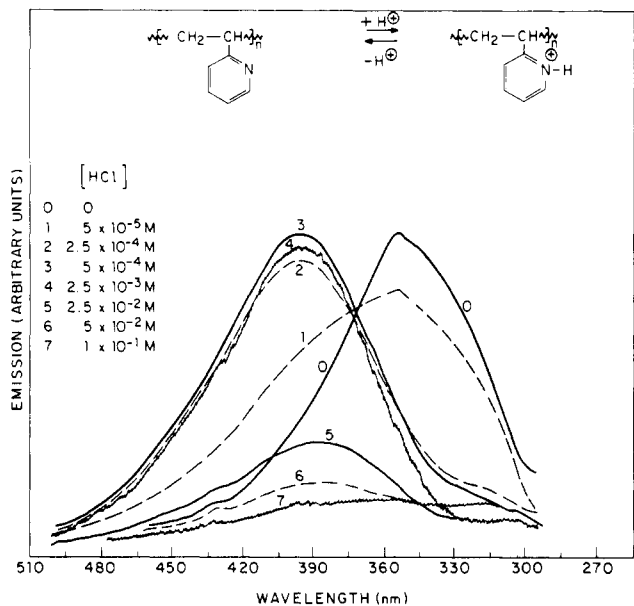
benzene-heptane and methanol-diethyl ether. Finally, it was freeze-dried from a dilute solution in benzene. The poly(ethylene oxide)-poly(propylene oxide) copolymer was purchased from the BASF Corp.

2-Ethylpyridine and standard 1 N solutions of HCl and NaOH were purchased from Aldrich Chemical Co. Solvents used were spectrograde or were distilled before use.

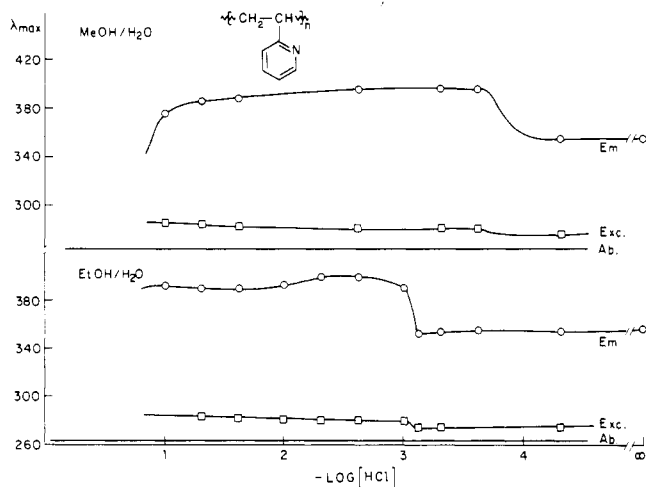
Absorption spectra were obtained on a Perkin-Elmer 559A spectrometer. Emission and excitation spectra were obtained on a Perkin-Elmer MPF-3L fluorometer. Fluorescence time correlated spectra were made on a single-photon counting system as described previously.<sup>20</sup> A filter solution was employed to select the excitation wavelength ( $\lambda < 280$  nm) and to minimize light scattering. The potentiometric titrations were performed with a Corning 130 pH meter at 20 °C. Calibration was made with standard buffer solutions at pH 4.00 and 7.01. All emission spectra were obtained in aerated solutions. Purging with nitrogen did not significantly alter the emission intensity.

## Results

**Dependence of P2VP Emission on Acidity.** Figure 1 shows the dependence of 50% methanol/50% water



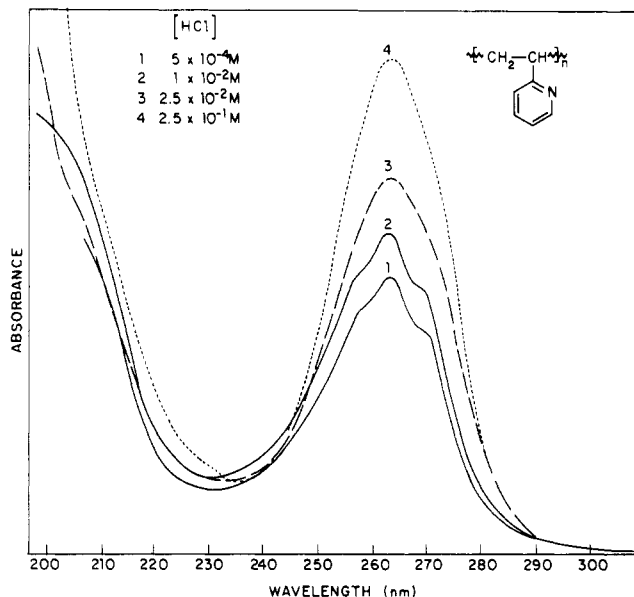
**Figure 1.** Emission spectra of P2VP in 50% methanol/water solution at different HCl concentrations: excitation wavelength, 260 nm; polymer concentration,  $2.1 \times 10^{-4}$  M.



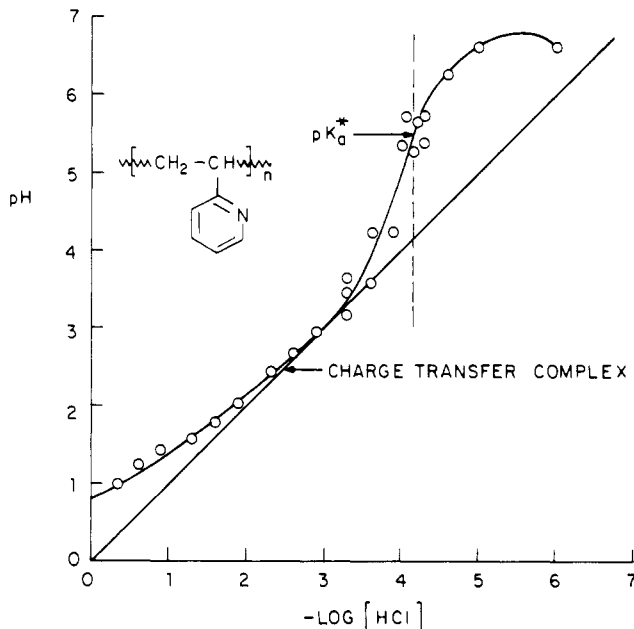
**Figure 2.** Maximum wavelength ( $\lambda_{\max}$ ) of the emission (Em), excitation (Ex), and absorption (Ab) spectra of P2VP in 50% alcohol/water solution as a function of HCl concentration: (a) methanol/water; (b) ethanol/water.

solutions of P2VP on the concentration of HCl. Three different domains are noted: (1) at relatively low concentrations of HCl P2VP emission maximizes at ca. 350 nm; (2) at intermediate concentrations of HCl the emission maximum of P2VP is shifted to ca. 390 nm; (3) at the highest concentrations of HCl the emission of P2VP is quenched. These results are summarized in Figure 2, which also displays data for the ethanol/water system. For both alcohol/water systems the maximum wavelength of the absorption and excitation spectrum of P2VP is not altered significantly by addition of HCl. However, the optical density of the P2VP solution increases with increasing acidity. For HCl concentrations greater than ca.  $10^{-2}$  M the vibrational resolution of the P2VP absorption disappears (Figure 3).

The observation of large ( $13\,500\text{ cm}^{-1}$ ) Stokes shifts of fluorescence maxima with varying pH may be readily interpreted in terms of emission from protonated and unprotonated species (Scheme I). Accordingly, the 350-nm emission of P2VP is assigned to the unprotonated polymer and the 390-nm emission of P2VP is assigned to the protonated polymer. The 390-nm emission of P2VP is ob-



**Figure 3.** Absorption spectra of P2VP in 50% ethanol/water solution at  $3.1 \times 10^{-4}$  M polymer concentration as a function of HCl concentration.



**Figure 4.** Dependence of pH of P2VP ( $1.4 \times 10^{-4}$  M) solution in 50% methanol/water on the concentration of HCl. In the figure are indicated the onset of charge-transfer complexation and the  $pK_a^*$  value as determined by eq 4 in the text.

served in aqueous solutions containing sufficient acid (HCl or  $\text{H}_2\text{SO}_4$ ) to bring the polymer into solution.

The degree of ground-state ionization,  $\beta$ , is defined by eq 1

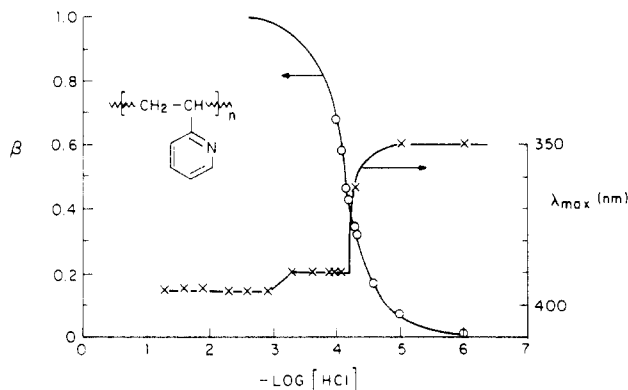
$$\beta = [\text{PH}^+]/([\text{P}] + [\text{PH}^+]) \quad (1)$$

where  $[\text{PH}^+]$  and  $[\text{P}]$  are the concentration of protonated and unprotonated monomer rings of P2VP. The quantity  $\beta$  may be determined experimentally by measuring the pH dependence of P2VP solutions on the concentration of HCl at a polymer concentration  $C$  and by the use of eq 2 and 3 (Figure 4).

$$[\text{PH}^+] = [\text{HCl}] - [\text{H}^+] \quad (2)$$

$$[\text{P}] = C - [\text{PH}^+] \quad (3)$$

In Figure 5 the dependences of both  $\beta$  and the emission maximum of P2VP are plotted against HCl concentration.



**Figure 5.** Variation of the ground-state degree of ionization ( $\beta$ ) and the maximum emission wavelength ( $\lambda_{\max}$ ) with the HCl concentration in P2VP ( $1.4 \times 10^{-4}$  M) solution in 50% methanol/water.

A sharp break in both plots is observed between  $10^{-4}$  and  $10^{-5}$  M HCl.

Ethylpyridine (EP) is virtually nonemissive in water or in water/alcohol mixture. The fluorescence emission of EP (under conditions comparable to those in Figure 1 for P2VP) is weak (maximum ca. 290 nm) and shows no significant pH dependence of the emission maximum.

## Discussion

P2VP is insoluble in neutral water, but is solubilized in acidic aqueous solutions or in neutral methanol/water mixtures. Even at very low HCl concentrations (at 1/100 of the polymer concentration) some of the rings of P2VP are protonated. As the concentration of HCl increases, the number of neighboring charged rings begins to increase. As a consequence of repulsive interactions between neighboring charged rings, the P2VP polymer coil expands and begins to assume a rodlike conformation. This conformational reorganization causes a decrease in the polymer basicity; i.e., after the conformational change it takes a larger concentration of HCl to protonate a monomer ring than it did before the conformational reorganization. From the literature,<sup>2</sup> it has been concluded that when one of five rings is protonated ( $\beta = 0.2$ ), the anionic counterions ( $\text{Cl}^-$ ) begin to partially associate with the polymer rings. We note that for  $0 < \beta < 0.4$  only the emission at 350 nm is observed. This emission is typical of P2VP in hydrogen-bonding solvents. Since 60% or more of the polymer rings are unprotonated under the condition  $0 < \beta < 0.4$ , we conclude that, when a protonated ring is electronically excited for this range of  $\beta$ , significant conformational changes occur and that proton transfer and/or hydrogen bonding to solvent molecules occurs (Scheme I). The reaction rate constant for proton transfer must be  $\geq 10^{10} \text{ s}^{-1}$ , since the equilibrium excited state is reached before emission.<sup>14</sup> As a result, only one emission band is observed (Figure 1), even though both protonated and unprotonated species exist in the ground state.

The absorption spectrum of P2VP is not significantly affected by protonation (Figure 3) except for a slight enhancement of the extinction coefficient (Table I). This result indicates that protonation affects only the  $n-\pi^*$  transitions and not the  $\pi-\pi^*$  transitions. Since a corresponding situation is observed for EP as for other heterocycles,<sup>15</sup> a polymer effect need not be invoked to interpret these data.

At  $\beta > 0.4$ , the 390-nm emission becomes dominant. This result is understandable in terms of Scheme I if it is assumed that excited neutral rings are protonated under these conditions so that emission only occurs from pro-

**Table I**  
Influence of  $\text{Na}_2\text{SO}_4$  ( $2 \times 10^{-2}$  M) on the Emission Intensity ( $I_F^{390}$ ) in Arbitrary Units and the Optical Density (OD) of a P2VP ( $1.4 \times 10^{-4}$  M) Solution in 50% Methanol in Water at Different HCl Concentrations

[HCl], M	without salt		with salt	
	OD	$I_F^{390}$	OD	$I_F^{390}$
$2.5 \times 10^{-3}$	0.40	53	0.425	70
$5 \times 10^{-3}$	0.435	46	0.465	63
$1.25 \times 10^{-2}$	0.47	31	0.55	57
$5 \times 10^{-2}$	0.53	28	0.58	42

tonated species. The acid concentration at which the shift from 350 to 390 nm occurs (Figure 2) depends on the solvent because the polymer  $\text{p}K_a$  and  $\beta$  vary with solvent dielectric constant.<sup>2</sup>

In small molecules, the pH at which the fluorescence of the protonated form begins is considered the  $\text{p}K_a$  of the first singlet excited state and is represented by  $\text{p}K_a^*$ . The  $\text{p}K_a$  of the ground state and  $\text{p}K_a^*$  are related by eq 4, derived by Weller<sup>16</sup> making use of the Forster cycle.<sup>17</sup>

$$\text{p}K_a - \text{p}K_a^* = (h\nu_A - h\nu_{\text{AH}})/2.3kT \quad (4)$$

In eq 4,  $k$  = Boltzmann's constant,  $h$  = Planck's constant, and  $\nu_{\text{AH}}$ ,  $\nu_A$  = frequencies of the peaking fluorescence of the acid and its conjugated base. This equation predicts for the P2VP a value of  $\text{p}K_a^*$  that is smaller than  $\text{p}K_a$  by 7  $\text{p}K$  units; i.e., it predicts that the first singlet state is a much weaker base than the ground state. That is in qualitative agreement with the experimental results, but a quantitative coincidence is not expected for at least two reasons: (1) When the difference of energy between the Franck-Condon and equilibrium energy levels is large (as is the case),<sup>1</sup> a correction must be applied to  $\nu_A$  and to  $\nu_{\text{AH}}$  for the relaxation of the solvent around the excited state; such corrections are not impossible to calculate quantitatively. (2) The value of  $\text{p}K_a$  in the case of polyions depends on the degree of ionization.<sup>18</sup>

In Figure 2, it can be seen that the excitation maximum wavelength undergoes insignificant variation relative to the much larger shift of the emission wavelength as the solution acidity is varied. These results support the idea that  $n-\pi^*$  transitions and not  $\pi-\pi^*$  transitions are responsible for the polymer fluorescence. No shift is observed in the absorption spectra, because the  $n-\pi^*$  absorption is hidden under the  $\pi-\pi^*$  band, which is the observed absorption. It has been suggested<sup>8</sup> that changes in the excitation spectra are indicative of ground-state equilibrium modifications, but in a polymer system different criteria have to be applied. In the case of small molecules, one of the two species in equilibrium in the ground state may appear or disappear by small changes in the medium pH, but in a polymer solution both the protonated and unprotonated forms coexist as long as some protonating agent is added, and the degree of ionization changes smoothly with the acid concentration. The small red shift in the excitation spectra shown in Figure 2 can be attributed to the stabilization of the protonated rings by partial condensation or site binding of the counterions to compensate for electrostatic repulsive interactions between too close, charged heterocycles.

When the degree of ionization is about 80%, a massive condensation of anions on the polymer chain produces a change in even the local monomer conformation as corroborated by NMR analysis.<sup>2</sup> It is also reflected in the loss of vibrational resolution in the absorption spectra (Figure 3).

For HCl, at large values of  $\beta$ , a charge-transfer complex forms between the protonated rings and chloride ions.

Although a new band is not observed in absorption (as is the case for iodide gegenions),<sup>19</sup> the quenching of P2VP emission (Figure 1) at high  $\beta$  can be attributed to charge-transfer quenching. It is expected that charge-transfer complexes can be destabilized or destroyed by addition of a salt. Indeed, upon addition of  $\text{Na}_2\text{SO}_4$  (Table I) to HCl-containing solutions of P2VP the emission intensity at 390 nm increases. This is explained as the result of the screening of electrostatic repulsions of neighboring protonated rings which relieves the need for gegenion condensation. The sulfate ions are not as effective as chloride ions at forming charge-transfer complexes and at quenching emission of the protonated rings.

It is rather remarkable that EP has no emission at 390 nm or at 350 nm. At HCl concentrations between 1 and  $10^{-7}$  M or in basic solutions, the EP emission is weak in intensity and maximizes at ca. 290 nm. The differences between P2VP and EP can be attributed to cooperative processes in the polymer or to specific local conformations of the monomer units forced by the polymer structure and that cannot be achieved by EP.

### Conclusion

The fluorescence emission properties of aqueous solutions and aqueous/alcohol solutions of P2VP are sensitive to pH changes. At low acidity near neutrality an emission (350 nm) characteristic of hydrogen-bonded pyridine rings is observed and at higher acidities an emission (390 nm) characteristic of protonated pyridine rings is observed. At still higher acidities studied all emission is quenched. Since the absorption spectra of P2VP do not change significantly with corresponding change in acidity, these results are explained in terms of structure features of the electronically excited polymer, in particular its conformation changes and acid-base properties.

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**Registry No.** P2VP (homopolymer), 25014-15-7; 2-ethylpyridine, 100-71-0.

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## Morphological Studies on the $\alpha$ and $\beta$ Structures of Isotactic Polystyrene

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**ABSTRACT:** The morphological features of films of isotactic polystyrene (iPS), crystallized by vapor exposure to hexahydroindan and cyclooctane, are described. Variations in the morphologies with the type of solvent, temperature, and duration of vapor exposure are illustrated. Vapor exposure to hexahydroindan at ambient temperature leads to the crystallization of the  $\beta$  structure with spherulitic morphology. Exposure at 35 °C causes cocrystallization of both  $\alpha$  and  $\beta$  structures. The smaller spherulites corresponding to the  $\alpha$  form appear as overgrowth on the large spherulites of the  $\beta$  structure, resembling a pincushion. Ringed spherulites, corresponding to the  $\beta$  structure, are seen upon exposure of iPS films to cyclooctane vapor at ambient temperature. At above ambient temperatures, e.g., at 27 °C, spherulites with single- and double-armed spirals are obtained. (Here  $\alpha$  refers to the threefold helical structure, and  $\beta$  to the crystalline form with the extended conformation of the chain.)

### Introduction

It has been shown before<sup>1,2</sup> that either the  $\alpha$  (threefold helical) or  $\beta$  (extended conformation) structure or both structures of isotactic polystyrene (iPS) can be crystallized from the bulk, by the technique of solvent-induced crystallization (SINC), with appropriate choice of solvent and

vapor exposure conditions. Although the  $\beta$  structure can be crystallized by the gelation route<sup>3,4</sup> the SINC method offers the advantage of crystallization at room temperature and hence the results are of interest in their own right. The cocrystallization of both  $\alpha$  and  $\beta$  structures from the bulk, by vapor exposure to hexahydroindan and cyclooctane, was described in the previous paper.<sup>2</sup> The equi-