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Effects of Acidity and Methylation on the UV and Fluorescence Spectra of Poly(pyridine)s in Aqueous Acidic Solutions and in the Solid State

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ABSTRACT: Poly(2,5-pyridine) and poly(3,5-pyridine) were synthesized by coupling polymerization of 2,5- and 3,5-dibromopyridine, respectively. Partially N-methylated poly(2,5-pyridine)s were prepared with a degree of N-methylation per repeating unit from 10 to 25%. UV spectra and fluorescence were studied in aqueous acidic solutions and in the solid state. The UV absorption maximum of poly(2,5-pyridine) is blue-shifted with increasing acidity and/or degree of N-methylation; however, the UV absorption maximum of poly(3,5-pyridine) does not change with the acidity of the solution. Fluorescence emission intensities of poly(2,5-pyridine) and poly(3,5-pyridine) increase with increasing acidity sharply up to *Ho* (Hammett acidity function) = −10.1. The fluorescence emission of poly(2,5-pyridine) is also enhanced by N-methylation. Protonated and N-methylated pyridines in poly(pyridine) are the fluorescence active species. The fluorescence emission maximum of poly(2,5-pyridine) shifts from 420 nm in dilute HCOOH solution to 520 nm in the solid state. Homogeneous films of poly(2,5-pyridine) with poly(vinyl alcohol) can be obtained by spin coating from the blended solutions. The longer wavelength emission (520 nm) which became dominant in blends containing more than 10 mol % of poly(2,5-pyridine) was assigned to an emission of excimer. However, when a highly protonated poly(2,5-pyridine) was blended with poly(vinyl alcohol), an intense 420 nm emission appeared and became dominant, since excimer formation was inhibited by intermolecular electrostatic repulsion. It is proposed that two blue electroluminescence (420 and 520 nm) devices based on poly(pyridine) can be constructed by varying the degree of protonation or N-methylation and controlling the composition of the blends of poly(2,5-pyridine) with appropriate polymers.

Introduction

Electroluminescence devices utilizing π-conjugated polyarylenes as emitting layers have become a subject of great interest since the first report of electroluminescence devices (ELDs) based on poly(phenylene−vinylene) (PPV) in 1990.[1] The application of conjugated polymers as active layers in ELDs offers several advantages such as low cost and easy processing by spin casting from solution. Another advantage is that the emitting wavelength can be chemically tailored.[2,3]

Recently, blue light-emitting diodes using poly(pyridine) (PPy) as the emitting layer were reported.[4,5] Polymers based on PPy offer some potential advantages over polymers based on poly(*p*-phenylene) (PPP). The preparation of the PPy is straightforward:coupling polymerization of 2,5-dibromopyridine using a metal catalyst.[6] The polymer is soluble in acidic solutions such as formic and dichloroacetic acid, thereby allowing spin casting directly from solution. The excitation and emission wavelengths may be varied by quaternization of the nitrogen atom. Preliminary results of an investigation of the effect of quaternization on the UV and fluorescence spectra of PPy are presented in this paper.

Experiment

Materials. 2,5-Dibromopyridine, 3,5-dibromopyridine, methyl iodide, anhydrous DMF, and 96% HCOOH were purchased from Aldrich Chemical Co. Poly(vinyl alcohol) ($M_w = 50\ 000$) was purchased from Polyscience Co. Deionized water and 96−98% H_2SO_4 were used.

Poly(2,5-pyridine) (2,5-PPy). A total of 9.47 g (40.0 mmol) of 2,5-dibromopyridine, **1**, 6.00 g (91.8 mmol) of activated Zn powder, 0.39 g (3.0 mmol) of anhydrous $NiCl_2$, 7.80 g (36.0 mmol) of triphenylphosphine, 0.30 g (3.0 mmol) of NaBr, and 90 ml of anhydrous DMF were added to a 250 mL flask with a stirring bar and capped by a rubber septum. Vacuum and argon gas were applied alternately to the flask by a three-way connector to remove any moisture and to fill the flask with argon. The reaction mixture was heated to 70 °C for 24 h. Red−brown color of active catalyst appeared during heating. After 24 h, the reaction mixture was cooled to room temperature and filtered. The resulting solid was washed with acetone and water and then dissolved in formic acid followed by reprecipitation with the addition of an aqueous NaOH solution. The precipitate was filtered, washed with water, ethanol, and acetone, and then dried under reduced pressure. A yellow and powdery material was obtained with a yield, of 2.62 g (85%). FT-IR (KBr pellet): 1586, 1458, 1010, 825, 787 cm^{-1}. ^{1}H-NMR (300 MHz): 8.85 (d), 8.20 (d), 7.85 (d), 7.20 (t) ppm.

Poly(3,5-pyridine) (3,5-PPy). Poly(3,5-pyridine) was prepared in a similar way except using 3,5-dibromopyridine instead of 2,5-dibromopyridine. FT-IR (KBr pellet): 1016, 882, 717 cm^{-1}. ^{1}H-NMR (300 MHz): 8.93 (s), 8.49−7.97 (m) ppm.

N-Methylated Poly(2,5-pyridine).[7] 2,5-PPy (1.0 g), 3.7 g of methyl iodide, 4 mL of methanol, and 4 mL of DMF were added to a 20 mL ampule. The ampule was sealed and heated to 80 °C for 4 h (sample 1) and for 2 days (sample 2). The reacting mixture was poured into 100 mL of acetone, and the precipitate was collected by filtration, washed with acetone, and dried under reduced pressure. The degree of N-methylation, controlled by reaction time, was 10 and 25% per repeating unit of 2,5-PPy for samples 1 and 2, respectively. ^{1}H-NMR (90 MHz): 9.8 (m), 9.2 (m), 8.7 (m), 8.2 (m), 4.8 (s), 4.6 (s) ppm.

Blend Films. Formic acid solutions of 2,5-PPy (concentration = 2.0 g/dL) and poly(vinyl alcohol) (concentration = 5.0 g/dL) were prepared. Homogeneous thin films were obtained by spin coating (3000 rpm and 60 s) of the blend solutions having different compositions.

Characterization. The inherent viscosity was measured in 96% formic acid at 25 ± 0.05 °C by an Ubbelohde viscometer. FT-IR spectra were obtained on a Perkin-Elmer 1600 FT-IR

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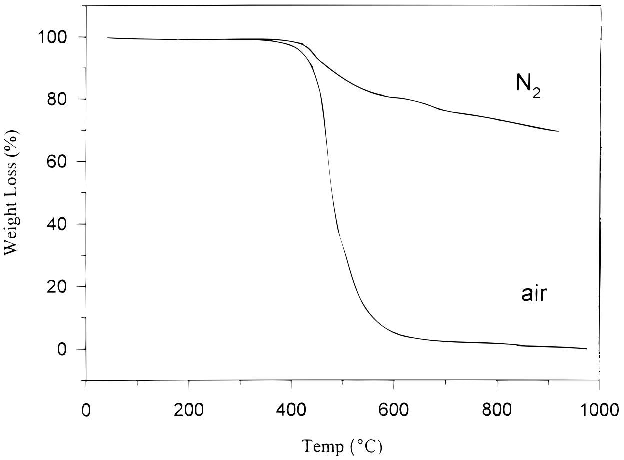

Figure 1. Thermal gravimetric analysis of poly(2,5-pyridine) with heating rate 20 °C/min under an air or N_2 atmosphere.

spectrophotometer. The degree of N-methylation was determined by ^{1}H-NMR using 20% DCl in D_2O for 2,5-PPy (Varian U-plus 300 MHz) and D_2SO_4 for the N-methylated polymer (Varian EM390 90 MHz). Thermal gravimetric analysis (TGA) experiments were performed using a Hi-Res TGA 2950 of TA Instruments with a heating rate of 20 °C/min under an air or nitrogen atmosphere. UV−vis absorption spectra were obtained using a Varian Cary 2300 UV−vis spectrophotometer with a 1.0 cm quartz cell. Fluorescence excitation and emission spectra were obtained using a Perkin-Elmer LS50B luminescence spectrophotometer. An L-format device was used for solution samples. Absorbance of all solution samples is controlled to 0.1 at the wavelength of excitation (λ_{ex}). λ_{ex} is 333 nm for the samples of 2,5-PPy in aqueous H_2SO_4 solutions ($Ho = -10.1, -7.34, -4.46$), 280 nm for all samples of 3,5-PPy, and 348 nm for the others. A 60/30° reflectance device was used for solid-state samples. Thicknesses of films were measured by Sloan Dektak II.

In order to quantify the protonating power of concentrated aqueous H_2SO_4, Hammett acidity function *Ho*[8] was used:

$$Ho = -\log([BH^+]/[B])$$

where $[BH^+]$ and [B] are protonated and nonprotonated bases, respectively. The aqueous solutions containing 97, 80, 60, 40, 20, and 10% H_2SO_4 have *Ho* values of −10.1,[9] −7.34, −4.46, −2.41, −1.01, and −0.31, respectively.

Results and Discussion

Characterization. The coupling polymerization of 2,5-dibromopyridine yielded various molecular weights of 2,5-PPy. The molecular weights of 2,5-PPy were reported in the literature[6] to be in the range of 2500−4000 with an inherent viscosity $\eta_{inh} = 0.85$ dL/g in formic acid (concentration = 1.0 g/dL) corresponding to a molecular weight of 3800. 2,5-PPy samples used in this study have inherent viscosities 0.68 dL/g in HCOOH (concentration = 1.0 g/dL). The polymer was thermally stable in air up to 400 °C and oxidized completely at 600 °C. However, under a nitrogen atmosphere the char yield was as high as 70% even at 1000 °C (Figure 1). The degree of N-methylation was controlled by varying the reaction time and was determined by ^{1}H-NMR spectroscopy (Figure 2). The peaks at 4.8 and 4.6 ppm with intensity ratios of approximately 3:1 are assigned to the *N*-methyl protons with different configurations. The broad and featureless peaks at 9.8 (m), 9.2 (m), 8.7 (m), and 8.2 (m) ppm are assigned to the protons on the pyridine ring with/without N-methylation. The degree of N-methylation was determined to be 10 and 25% per repeating unit of 2,5-PPy with reaction times of 4 h and 2 days at 80 °C, respectively.

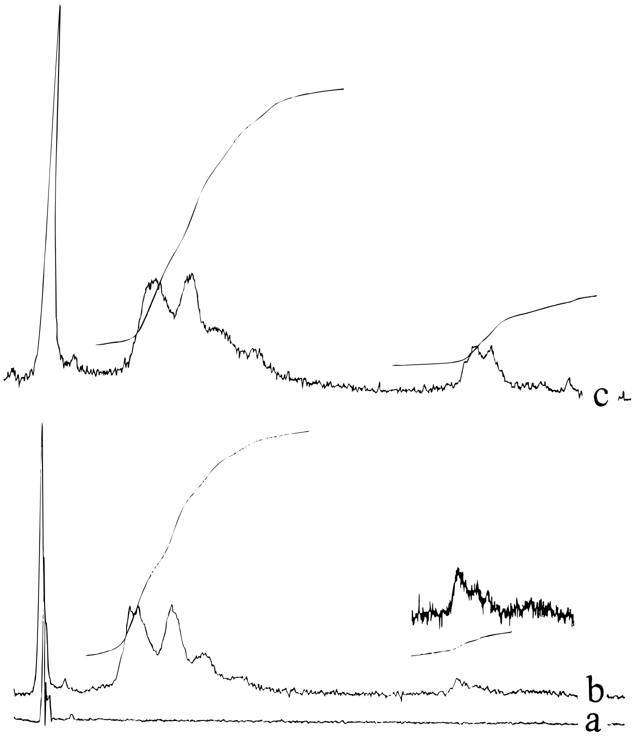

Figure 2. ^{1}H-NMR spectra of partially N-methylated poly(2,5-pyridine) in D_2SO_4: (a) D_2SO_4, (b) 10% N-methylated 2,5-PPy, and (c) 25% N-methylated 2,5-PPy.

Table 1. UV Absorption of Poly(2,5-pyridine) and Partially N-Methylated Poly(2,5-pyridine) in Aqueous Acidic Solutions

polymer	solvent (*Ho*[a])	λ_{max} (nm)	log ϵ_{max} (M^{-1} cm^{-1})
2,5-PPy	aqueous H_2SO_4 (−10.1)	330	3.74
	aqueous H_2SO_4 (−7.34)	333	3.79
	aqueous H_2SO_4 (−4.46)	335	3.74
	aqueous H_2SO_4 (−2.41)	345	3.73
	aqueous H_2SO_4 (−1.01)	348	3.77
	aqueous H_2SO_4 (−0.31)	349	3.74
	HCOOH	354	3.88
25% *N*-Me 2,5-PPy	HCOOH	348	3.92
10% *N*-Me 2,5-PPy	HCOOH	352	3.91

[a] Hammett acidity function (*Ho*) from refs 8 and 9.

UV Absorption. The UV absorption spectra of 2,5-PPy and partially N-methylated 2,5-PPy were obtained in aqueous acidic solutions, and typical data are summarized in Table 1. A broad absorption band at 345 ± 15 nm was found in the scanning range from 250 to 550 nm. The strong absorption band (molar extinction coefficient: log $\epsilon_{max} = 3.7-4.0$ M^{-1} cm^{-1}) is due to a $\pi-\pi^*$ transition of the conjugated 2,5-PPy backbone.[6] The wavelength of absorption maxima (λ_{max}) is blue-shifted with increasing acidity or upon N-methylation. The blue shift of λ_{max} starts abruptly at around $Ho \sim -4.0$. On the other hand, the effect of acidity on the molar extinction coefficient is very small. 2,5-PPy dissolves only in acids, such as HCOOH, $Cl_2CHCOOH$, and H_2SO_4, and the degree of protonation of the nitrogen atom depends on the acidity of the solution. Nakamoto[10] reported that the dication of 2,2′-bipyridyl exists only in extremely strong acids because of electrostatic repulsion between the two adjacent cations; for the same reason, the trication of 2,2′,2″-terpyridyl cannot be found even in a 5 M aqueous H_2SO_4 solution. The coupling

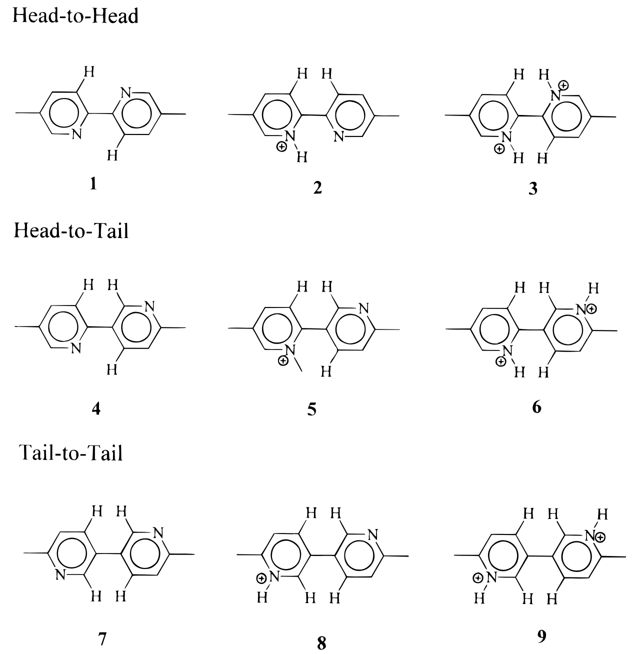

Figure 3. Dimeric units of poly(2,5-pyridine) with/without protonation: head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT).

polymerization of 2,5-dibromopyridine yielded chain molecules with head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) units, the HT unit being much more frequent.[6] Figure 3 illustrates the three units of 2,5-PPy with/without protonation. Biphenyl exhibits a torsional angle of approximately 42° between the planes of the rings in the vapor state and an angle of approximately 23° in the melt.[11] When one C−H group on each ring is replaced by a nitrogen atom, some of steric hindrance involving the ortho-hydrogen is alleviated and the torsional angle is decreased to less than 10°.[12] The abundance of each dimeric unit in 2,5-PPy can be roughly estimated by the pK_a values[13] of 2,2′-bipyridyl (4.25, −0.15), 2,3′-bipyridyl (4.40, 1.50), and 3,3′-bipyridyl (4.60, 3.00), which correspond HH, HT, and TT units, respectively. Thus, nonprotonated dimeric units **1, 4,** and **7** exist in negligibly small quantities in acidic solutions ($-10.1 < Ho < -0.31$). Monoprotonated dimeric units **2, 5,** and **8** are the dominant species in solutions having weak to intermediate acidities, and diprotonated dimeric units **3, 6,** and **9** exist only in strongly acidic solutions. According to the Figure 3, it is expected that monoprotonation in 2,5-PPy leads to an increase in the steric hindrance between the N-proton and the ortho-hydrogen. The severe steric and Columbic interactions of the diprotonated dimeric units lead to further ring twisting, and decreasing coplanarity of the pyridine rings results in the blue shift of 2,5-PPy. The blue shift of λ_{max} of partially N-methylated 2,5-PPy can be understood on the same basis. These results are consistent with the previous finding by Yamamoto et al.,[6] who reported that alkyl substitution on 2,5-PPy caused a shift of the $\pi-\pi^*$ transition to shorter wavelengths by 30−60 nm. The prominent blue shift in the neighborhood of $Ho \sim -4.0$ was presumably caused by the transformation from the monoprotonated to the diprotonated dimeric unit.

The UV absorption spectra of poly(3,5-pyridine) (3,5-PPy) in aqueous acidic solutions are summarized in Table 2. Two strong absorption bands were found, shorter wavelength absorption $\lambda_{max} = 230 \pm 2$ nm (log $\epsilon_{max} = 4.01 \pm 0.02$ M^{-1} cm^{-1}) and longer wavelength absorption $\lambda_{max} = 280 \pm 2$ nm (log $\epsilon_{max} = 3.78 \pm 0.04$ M^{-1} cm^{-1}). The results are quite similar to those of 3,3′-bipyridyl,[14] which also has two absorption bands at $\lambda_{max} = 229$ nm (log $\epsilon_{max} = 4.10$ M^{-1} cm^{-1}) and $\lambda_{max} = 279$ nm (log $\epsilon_{max} = 3.78$ M^{-1} cm^{-1}). The longer wavelength absorption (280 nm) of 3,5-PPy had a larger blue shift than 2,5-PPy (345 ± 15 nm), but the locations of the two absorption maxima in the 3,5-PPy spectra were not influenced by the acidity of the solution. These differences in the UV absorptions between 2,5-PPy and 3,5-PPy are due to a difference of conjugation along the poly(pyridine) backbone. In the case of 3,5-PPy, resonance contribution from neighboring pyridine rings is much smaller than in 2,5-PPy. Thus, the positive charge on the nitrogen atom of 3,5-PPy is localized mainly in the pyridine rings, and the absorption of 3,5-PPy could be treated as the sum of this absorption. The resemblance of absorption spectra between 3,5-PPy and 3,3′-bipyridyl as well as the independence of the absorption maxima of 3,5-PPy on acidity can be understood on this basis.

Table 2. UV Absorptions of Poly(3,5-pyridine) in Aqueous Acidic Solutions

polymer	solvent (Ho^a)	λ_{max} (nm)	log ϵ_{max} (M^{-1} cm^{-1})
3,5-PPy	aqueous H_2SO_4 (−10.1)	278	3.76
		229	4.00
	aqueous H_2SO_4 (−7.34)	279	3.80
		230	4.03
	aqueous H_2SO_4 (−4.46)	279	3.82
		230	4.03
	aqueous H_2SO_4 (−2.41)	278	3.76
		232	4.03
	aqueous H_2SO_4 (−1.01)	280	3.74
		232	4.01
	HCOOH	280	3.81
		^{b}	

[a] Hammett acidity function (Ho) from refs 8 and 9. [b] The cut-off wavelength of HCOOH is 260 nm.

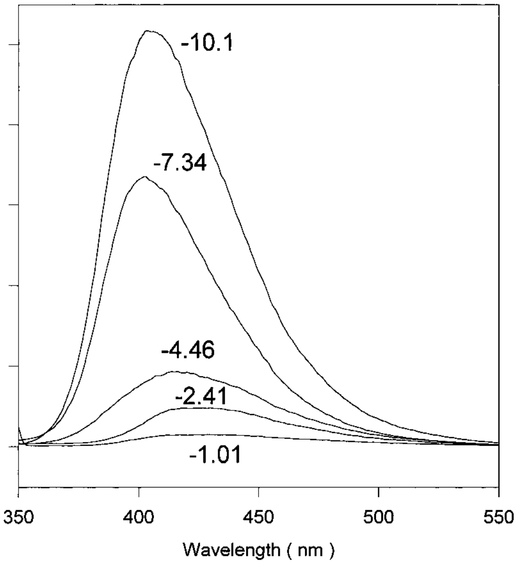

Figure 4. Fluorescence emission spectra of poly(2,5-pyridine) in aqueous sulfuric acid solutions. Numbers are acidities in *Ho* scale.

Fluorescence Excitation/Emission. The fluorescence emission spectra of 2,5-PPy in aqueous acidic solutions are shown in Figure 4 and summarized in Table 3. The emission maximum of 2,5-PPy shifts to shorter wavelengths with increasing acidity. This blue shift is caused by an increasing torsional angle between

Table 3. Fluorescence Excitations and Emissions of Poly(2,5-pyridine) and Partially N-Methylated Poly(2,5-pyridine) in Aqueous Acidic Solutions

		λ_{max} (nm)	
polymer	solvent (*Ho*[a])	excitation	emission
2,5-PPy	aqueous H_2SO_4 (−10.1)	337	405
	aqueous H_2SO_4 (−7.34)	337	405
	aqueous H_2SO_4 (−4.46)	337, 354	415
	aqueous H_2SO_4 (−2.41)	354	415−430[b]
	aqueous H_2SO_4 (−1.01)	354	415−430[b]
	aqueous H_2SO_4 (−0.31)	*c*	415−430[b]
	HCOOH	355	415, 430
25% *N*-Me 2,5-PPy	HCOOH	350	415, 430
10% *N*-Me 2,5-PPy	HCOOH	350	415, 430

[a] Hammett acidity function (*Ho*) from refs 8 and 9. [b] In these cases, a broad wavelength range of maximum emission was observed. [c] No distinct excitation maximum is observed.

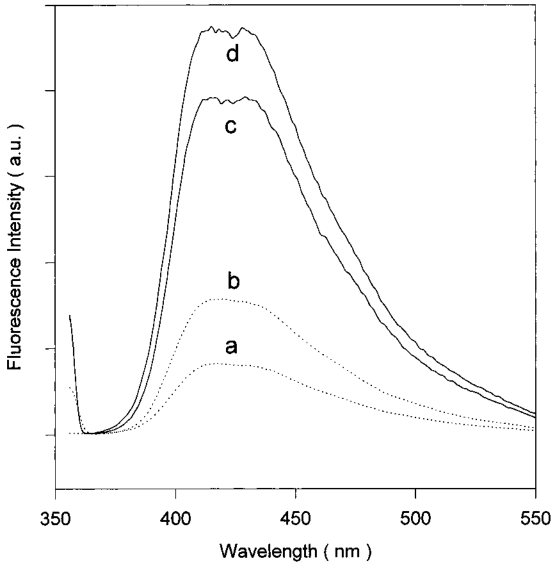

Figure 5. Fluorescence emission spectra of poly(2,5-pyridine) in formic acid: (a) poly(2,5-pyridine), (b) a + 0.1 M *p*-toluenesulfonic acid, (c) 10% N-methylated poly(2,5-pyridine), and (d) 25% N-methylated poly(2,5-pyridine).

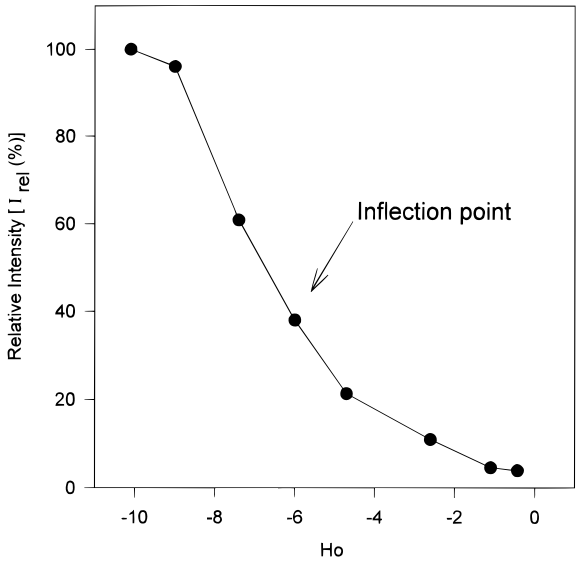

Figure 6. Relationship between the relative fluorescence emission intensity (I_{rel}) of poly(2,5-pyridine) and the acidity (*Ho* scale) of the aqueous sulfuric acid solutions.

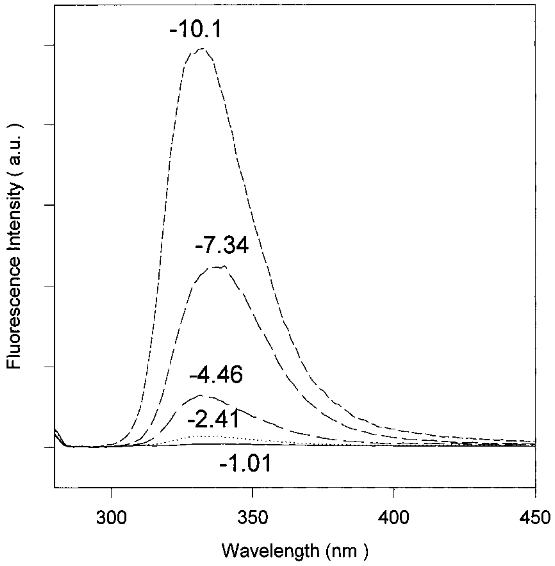

Figure 7. Fluorescence emission spectra of poly(3,5-pyridine) in aqueous sulfuric acid solutions. Numbers are acidities in *Ho* scale.

the planes of the rings as discussed in the section on UV absorption. The emission intensity of 2,5-PPy increases with increasing acidity sharply up to $Ho = -10.1$.[15] The emission intensity of 2,5-PPy in a 97% aqueous H_2SO_4 solution ($Ho = -10.1$) was found to be 30 times higher than that in a 10% aqueous H_2SO_4 solution ($Ho = -0.31$). In addition, when 0.1 M of *p*-toluenesulfonic acid was added to a HCOOH solution of 2,5-PPy, the fluorescence intensity was increased 2-fold (Figure 5). Pyridine and its derivatives are known to be nonfluorescent, but they fluoresce when protonated.[15,16] Thus, in the case of poly(pyridine), it can be concluded that the protonation is the dominant factor in fluorescence emission and the intensity was found to increase with increasing acidity of the solution (Figure 6). The fluorescence intensity of 2,5-PPy in HCOOH was enhanced by N-methylation. Especially, the fluorescence intensity of 25% N-methylated 2,5-PPy was almost 6-times higher than that of 2,5-PPy (Figure 5). The increase in the fluorescence intensity of 2,5-PPy depends on the extent of the N-methylation. Fluorescence emission spectra of 3,5-PPy in aqueous acidic solutions are shown in Figure 7. The emission maximum (330 nm) does not change with varying acidity and is consistent with the invariance of the absorption maximum of 3,5-PPy (280 nm). However, fluorescence intensity increases with increasing acidity in a way similar to 2,5-PPy.

In fluorescence excitation spectra of 2,5-PPy, two bands were found at around $Ho = -4.46$ as shown in Figure 8, which corresponds to the inflection point in Figure 6. Similar inflection points were reported[15] for the 2,2′-bipyridyl at $Ho = -7.8$ (in aqueous H_2SO_4) and at $Ho = -5.8$ (in $HClO_4$). The two bands which are located at 337 and 354 nm correspond to the excitation maxima of 2,5-PPy in higher acidity ($Ho < -5.0$) and lower acidity ($Ho > -4.0$) media, respectively. This indicates that two excitation modes coexist which presumably correspond to diprotonated and monoprotonated dimeric units. The tacticity of 2,5-PPy may not be responsible for the two excitations, because the two emissions are only observed in the sample at $Ho = -4.46$, and an identical emission is observed by either excitation at $\lambda_{ex} = 337$ or 354 nm. At higher acidity, the diprotonated units predominate and the spectra exhibit only one band with an excitation maximum at 337 nm. However, the proportion of monoprotonated

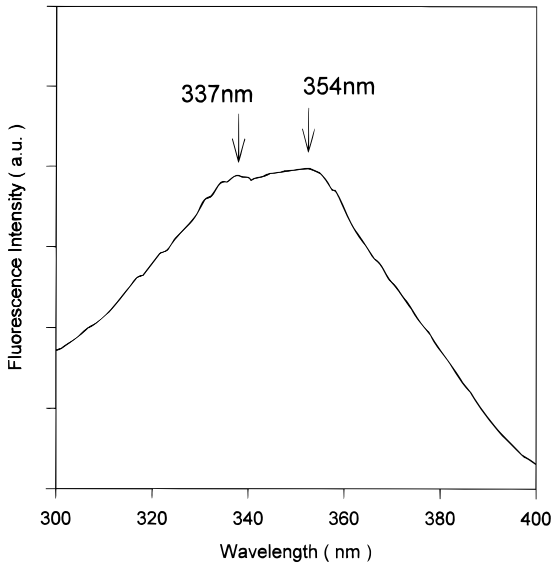

Figure 8. Fluorescence excitation spectrum of 2,5-PPy in aqueous sulfuric acid solution ($Ho = -4.46$).

dimeric units increases in lower acidity media, and only one band appears at 354 nm. The reason why the two excitations give a single emission is not clear. One of possible reasons is due to the rapid deprotonation from the diprotonated species to the monoprotonated species in the excited state which is much faster than emission from the diprotonated species.[15] This is supported by the observed value of the emission maximum of 2,5-PPy at $Ho = -4.46$ (415 nm) which is closer to that of 2,5-PPy in a weak acidic medium ($Ho > -4.0$) than that of 2,5-PPy in a strong acidic medium ($Ho < -5.0$).

A thin film (thickness = 0.5 μm) of 2,5-PPy was prepared by spin coating of the HCOOH solution. The fluorescence emission spectrum of the film has a maximum at 520 nm instead of that at 420 nm in solution. This was attributed to an excimer type emission.[5,17] In order to further elucidate the excimer formation in 2,5-PPy, blend films (thickness = 2 ± 0.5 μm) of 2,5-PPy with PVA were prepared. The emissions at 420 nm decreased sharply with an increasing amount of 2,5-PPy in the blend (Figure 9). Blend films containing more than 10 mol % of 2,5-PPy showed only the excimer emission at 520 nm. However, when the blended films of the same compositions were cast from HCOOH solution containing as little as 0.1 M *p*-toluenesulfonic acid, an intense 420 nm emission appeared and became dominant over the excimer emission (Figure 10). This suggests that when the positive charge on the nitrogen atoms in 2,5-PPy reaches a critical value, the intermolecular electrostatic repulsion prevents excimer formation. However, the existence of a broad shoulder emission extending to 550 nm (Figure 10b) implies that excimer is not completely inhibited; that is, excimer and single fluorophore coexist, the latter being dominant. Therefore, the previously reported greenish blue electroluminescence devices were based on the excimer emission of polypyridine.[4,6] Using the same polymer, an effective blue light emitting (420 nm) diode may be constructed using highly protonated poly(pyridine) or a blend with PVA (concentration of 2,5-PPy < 1.0 mol %).

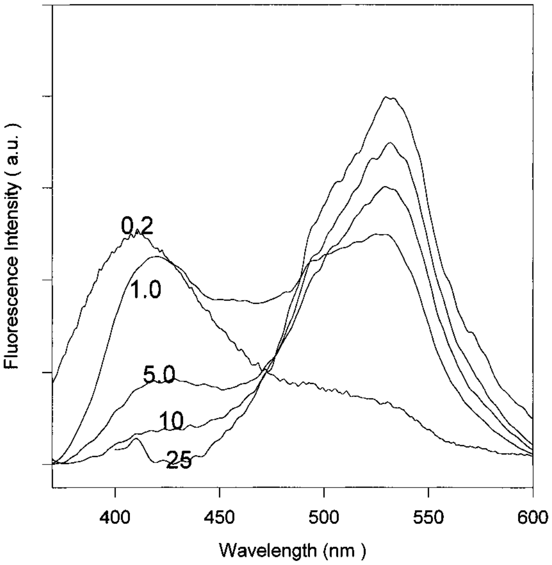

Figure 9. Effect of concentration of poly(2,5-pyridine) in the films of poly(2,5-pyridine)/poly(vinyl alcohol) blends on the fluorescence emission spectra. Numbers are mol % poly(2,5-pyridine) in the blends.

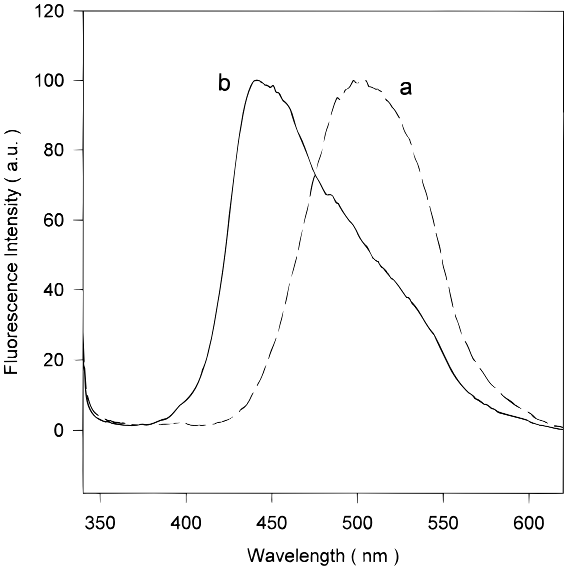

Figure 10. Normalized fluorescence emission spectra of the films of 10 mol % poly(2,5-pyridine) in poly(2,5-pyridine)/poly(vinyl alcohol) blends: (a) casting from formic acid and (b) casting from formic acid containing 0.1 M *p*-toluenesulfonic acid.

Conclusion

Poly(2,5-pyridine), poly(3,5-pyridine), and partially N-methylated poly(2,5-pyridine)s (10 and 25% per repeating unit) were synthesized. Blue shift of UV absorption maximum was found not only by an increase of the acidity of the aqueous solutions but also on N-methylation of poly(2,5-pyridine). The blue shift of the UV absorption maximum of N-protonated and/or N-methylated poly(2,5-pyridine) was caused by a decreasing coplanarity of the pyridine residues. However, UV absorption maximum of poly(3,5-pyridine) did not change with acidity. The fluorescence emission intensities of poly(2,5-pyridine) and poly(3,5-pyridine) depended strongly on acidity, increasing sharply at $Ho = -10.1$. N-Methylation of poly(2,5-pyridine) also enhanced the emission intensity. Protonated and N-methylated pyridines in poly(pyridine)s are the fluorescence active species. Two emissions were found in films of poly(2,5-pyridine)/poly(vinyl alcohol) blends. The longer wavelength emission (520 nm) is due to an excimer, and the short wavelength emission (420 nm) is the typical emission of protonated poly(2,5-pyridine) in solution. The two emissions can be easily modulated. The shorter wavelength emission (420 nm) completely disappeared in the blends containing more than 10 mol % poly(2,5-pyridine). The emission of excimer (520 nm) disappeared by protonation of poly(2,5-pyridine) or in the blend containing less than 1 mol % poly(2,5-pyridine).

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