Photo-induced Surface Protonation and Fast-scanned Luminescence Spectra of Poly(4-vinylpyridine) in Solid

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Pyridines are known to have different pK_a in the excited state from pK_a in the ground state. They are easily protonated in their photo-excited states. In previous studies, we reported the luminescence properties of thin films of a pyridine-containing polymer, poly(4-vinylpyridine)(P4VPy). In this study, the changes in emission spectra of bulk solid and thin films of P4VPy with UV-irradiation are reported, and the influence of the film thickness of P4VPy is re-examined taking the effect of surface protonation into consideration. Though protonation of P4VPy has been reported many times, and the proton source are inside of the polymer, the surface protonation of P4VPy in this study are caused by the extrinsic, outer proton sources.

Keywords: pyridine, hydrogen bond, polymer surface modification, luminescence, photo-induced protonation

1. Introduction

We had reported[1-3] the quaternization of pyridines(**1**; Py)(see **Scheme 1**) to alkyl- or other hydrocarbon-substituted pyridiniums(**2**; Py^+R)(see **Scheme 2**) with halogenated hydrocarbons(**3**; RX) using thin films of a polymeric pyridine derivative, poly(4-vinylpyridine)(**4a**; P4VPy). Pys(**1**) had been investigated by many scientists[for example, refs. 4-10 and the references cited in refs [1-3].

Scheme 1. Quaternization of Pys(**1**)

In our previous studies, we used thin films of P4VPy(**4a**). P4VPy(**4a**) was found to be easily “surface-quaternized” to its alkylpyridinium derivative(**5**; $PVPy^+R$; $R \neq H$) to some extent of the surface[1,2]. Although only the surface layer of the films could be quaternized, absorption and emission spectra were significantly changed with the exposure to various kinds of halogenated hydrocarbons(**3**), such as ethyl bromide(**3a**; EtBr).

Scheme 2. Quaternization of P4VPy (**4a**)
(x : the extent of quaternization)

The absorption spectra of the spin-coated thin films of P4VPy(**4a**) were similar to those of poly(vinylpyridine)s(**4**; PVPys) in solutions and gels in the previous studies[11-19]. Furthermore, it had been recently revealed that absorption and luminescence spectra of PVPys(**4**) were influenced with a several minute-irradiation, despite the low intensity of the 260 nm excitation light of the fluorescence spectrometer. In addition, our equipments was found to have some trouble in optical system of the fluorescence spectrometer used in our previous reports[1-3], especially in UV-C ($\lambda < 300$ nm) region[3].

In this study, we reported the corrected fast-scanned emission spectra of P4VPy(**4a**) thin films which were used in previous report[3] with a fast-scanning fluorescence spectrometer. The spectral changes in absorption and emission of

P4VPy(**4a**) with irradiation at 254 or 260 nm were also reported at the same time. In the absorption spectra of P4VPy(**4a**), an absorption band which contains a few small shoulders was seen ($\lambda_{\text{max.}} \sim 257$ nm) for all films[1-3]. It was assigned to the monomer (Py(**1**)) band, and the structure of the band was explained that both of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions located in the same region[6-9].

Because of the complexity of the transition, the luminescence property of P4VPy(**4a**) is much complicated[6-9]. Pirola *et al.* reported that UV-irradiation ($\lambda < 280$ nm) of PVPys(**4**) in solutions causes the excited state proton-transfer [11-14] of PVPys(**4**) to form protonated-pyridine(**6**; Py⁺H) moieties, because of the difference between the pK_a and pK_a^* as the common property of Pys(**1**) and PVPys(**4**). They also reported the ground- and excited-state equilibria for poly(2-vinylpyridine)(**4b**; P2VPy) in the presence of hydrochloric acid[11].

Formulae 1. Structures of the protonated pyridine(**6**), protonated P4VPy (**7a**) and hydrogen-bonded P4VPy (**8a**) (x : the extent of protonation)

It was mentioned that Py(**1a**) has a relatively high $pK_a(\sim 5.23)$ [6] and low $pK_{\text{HB}}(\sim 1.86)$ [19] in the ground state. Pys(**1**) moieties in the polymer chains of PVPys(**4**) are seemed to exist as hydrogen-bonded in the ground state. In alcoholic/aqueous solution of PVPy(**4**), protonated PVPy(**7**; PVPy⁺H) (for P4VPy(**4a**): P4VPy⁺H(**7a**); see **Formulae 1**) would not be seen in the absorption and emission spectra of dilute solutions of P4VPy(**4a**)[12-14] in the absence of acid. For P2VPy(**4b**)[11], the same phenomena were also observed in dilute solutions in the absence of acid. From these results, PVPy⁺H(**7**) seemed to exist only in acidic solutions[11-14]. In the absorption spectra, the band around 255 nm of P4VPy(**4a**) decreased and the weak absorption foot shifted from UV to visible region after complexing with acids[14]. Because of the high hydrogen bond basicity[19], Pys(**1**) moieties in the P4VPy (**4a**) chain would be complexed with hydrogen of acids, water and other hydrogen bond donors to form hydrogen-bonded PVPys(**8**; PVPy $\cdots$ H, for P4VPy (**4a**): P4VPy $\cdots$ H(**8a**)). Though Pirola *et al.* and other groups reported the excited-state proton transfer in dilute solution[11-15], Vaganova *et al.*

observed some new absorption and emission band in concentrated viscous solutions and in gels of P4VPy(**4a**) and Py(**1a**). They assigned the new bands as the hydrogen bond complexes of P4VPy(**4a**) with Py(**1a**) or other hydrogen bond donors[16-19]. The opposite results to those in dilute solutions had been obtained in gels and viscous solutions.

While the required time for the luminescence spectra of P4VPy(**4a**) thin films in our previous studies was 10 min or longer, as described above, there would be the possibility of the emission spectra ($\lambda_{\text{ex.}} = 260$ nm) in our previous study[3] being affected by the formation of P4VPy⁺H(**7a**). The correct luminescence spectra of P4VPy(**4a**) were determined with fast-scanning in this study. In addition, the effect of UV-irradiation on P4VPy(**4a**) thin films and bulk solid were also examined and the results were discussed.

2. Experimental

2.1. Materials and Sample Preparation

Solid pieces of P4VPy(**4a**) (Sigma Aldrich Co.) were dried over 140 °C under deaerated condition after reprecipitation from methanol to diethyl ether. Thin films of PVPy(**4a**) were prepared from the above reprecipitated polymer.

UV spectral grade methanol (Dojindo Molecular Technologies, Inc.) and HPLC grade diethyl ether (Wako Pure Chemical Industries, Ltd.) were used as supplied. The sample films were prepared with the spin-coating method. The highest concentration of methanolic polymer solution was ~ 0.5 g / ~ 5 mL, and gradually diluted with methanol to obtain various thickness of P4VPy(**4a**) films. P4VPy (**4a**) solution was dropped on the cleaned glass plates on the spin-coater and coated P4VPy(**4a**) at 1500 rpm for 60 s, and the films were dried over T_g under deaerated conditions.

Though the precise concentration is unknown, the thickness of the films were checked with absorption spectra[3]. P4VPy(**4a**) films showed an absorption band around ~ 260 nm which has a few peaks[12-14]. Each absorbance at 257 nm was 2.69, 1.00, 0.499, 0.262 for films No.1 $\sim$ No.4, respectively (the absorbance of synthetic quartz substrate = 0.034)[3].

No.1 film was the thickest film and was used for the experiment of the effect of UV-irradiation. All sample films were kept in an auto-desiccator (As One Corp.; inside of the case is kept at 20 $\sim$ 30 % humidity). The room temperature was ~ 25 °C, and the humidity was 50 $\sim$ 60 %.

2.2. UV-irradiation of bulk solid and No.1 thin film of P4VPy(4a).

The thin film of P4VPy(4a) (film No.1 in previous section) was irradiated with a small Hg lamp filtered at 254 nm ($\sim 4 \mu\text{W} / \text{cm}^2$). The bulk solid of P4VPy(4a) was irradiated with a 150 W Xe-lamp monochromated at 260 nm ($\sim 0.1 \mu\text{W} / \text{cm}^2$), with the internal light of F-4500 fluorescence spectrophotometer. In the case of P4VPy(4a) thin film (No.1), $\Delta \text{Abs.}$ with irradiation was ~ 0.02 over the wavelength range of measurement, even though the irradiation at 260 nm for 10 min was carried out using 150 W Xe-lamp. With this result, the required time for the fast-scanning (within 1 min) was sufficiently short to neglect the effect of the formation of P4VPy⁺H(7a). To determine the luminescence spectra of P4VPy(4a), each spectrum was measured within a few ten seconds or up to 1 min using fast-scanning, hereafter.

Irradiation time was 10 min in every case. The absorption spectrum of P4VPy(4a) was determined before irradiation, immediately after the irradiation, and after subsequent 1 day annealing. The sample film was kept in dark under dry conditions (in an auto-desiccator). Peak fitting had done with software "PeakFit" (SYSTAT Software Inc.).

2.3. Measurements of Optical Properties of P4VPy(4a) thin films and bulk solid

UV-visible absorption spectra were measured with a double beam UV-visible spectrophotometer, UV-3200 (Hitachi Ltd.). For the luminescence spectra, an F-4500 fluorescence spectrophotometer (Hitachi Ltd.) was employed. The luminescence spectra of P4VPy(4a) thin films were recorded with 2400 nm / min or faster scanning to avoid photo-induced reaction of P4VPy(4a). Emission decay curves were determined with NAES-1100S and were analyzed with "FluoFit" software (Pico Quant GmbH). A plate of synthetic quartz was placed slantingly in the cuvette holder for determination. Excitation light was H₂-flash lamp, filtered with a 1 cm quartz cuvette containing CuSO₄ aqueous solution (transparent to 300 ~ 600 nm) and color glass filters.

3. Results

3.1. The Effect of UV-irradiation : (1) P4VPy(4a) thin films.

Though the thin film was completely colorless before irradiation, it was colored in transparent yellow after irradiation. The change in the absorption spectrum was determined (Fig. 1).

With irradiation, the monomer (Py(1)) band around 255 nm was decreased ($\Delta \text{Abs.}(1)$ in Fig. 1a) and $\Delta \text{Abs.}$ in Fig. 1b)), and two new bands 300 and 390 nm appeared. One day after the irradiation, these two bands were vanished. $\Delta \text{Abs.}(2)$ in Fig. 1a) depicted that the increase around 255 nm (the monomer (Py(1)) band) simultaneously occurred with the decrease of the two new bands.

Fig. 1. Spectral change of film No.1 with 10 min irradiation at 254 nm.

The lines correspond to the absorbance before irradiation (---), after irradiation (—), after subsequent 1 day annealing (···), and the difference ($\Delta \text{Abs.}(1)$ in Fig. 1a) and $\Delta \text{Abs.}$ in Fig. 1b)) between before and after irradiation (—) and the difference ($\Delta \text{Abs.}(2)$ in Fig. 1a)) between after irradiation and after annealing (···).

These changes with UV-irradiation / annealing were summarized in Table 1.

The changes in emission spectra were determined simultaneously. Decrease in the emission intensity ($\Delta \text{Em.}$) in each case was shown in Fig. 2.

Table 1. $\Delta \text{Em.}$ of film No.1 with UV-irradiation and subsequent 1 day annealing.

$\lambda_{\text{ex.}} / \text{nm},$ status	correspondent Fig. / legend	$\lambda_{\text{max.}}^{\S}$ / nm	$\lambda_{\text{min.}}^{\P}$ / nm
260, irradiated	2a) / $\Delta \text{Em.}(a)$	340	425
260, annealed	2a) / $\Delta \text{Em.}(b)$	335 [†]	370
260, total	-	335	420 [†]
300, irradiated	2b) / $\Delta \text{Em.}(a)$	355, (460 [†])	-
300, annealed	2b) / $\Delta \text{Em.}(b)$	320	465
300, total	-	320, 470	375 [†]

[§] $\lambda_{\text{max.}}$ corresponds to the wavelength of the largest decrease, and [†] $\lambda_{\text{min.}}$ does to that of the smallest decrease.

[†] shoulder., [†] decrease was ~ 0 .

Emission spectra were recorded with excitation light at 260 and 300 nm (see Fig. 2 a) and b)).

$\lambda_{\max}$ of decrease were located at ~ 335 nm (in Fig. 2a)) and ~ 355 nm (in Fig. 2b)). $\lambda_{\min}$ of decrease (or $\lambda_{\max}$ of increase) appeared at ~ 420 nm (in Fig. 2a)) and ~ 365 nm (in Fig. 2b)). In the case of 260 nm irradiation and subsequent 1 day annealing, the shorter part of the monomer (Py(1)) emission band around ~ 335 nm would decrease with total processes. On the other hand, in the case of 300 nm irradiation and subsequent 1 day annealing, not only the shorter part of the monomer (Py(1)) emission band, but the longer emission band which correspond to another emission band should decrease. The amount of emission might decrease in each case.

Fig. 2. Changes in the emission spectra excited at a) 260 nm and b) 300 nm of film No.1 with UV-irradiation and subsequent 1 day annealing. ΔE_m : decrease in emission intensities, (a): decrease with UV-irradiation, (b): decrease with annealing.

3.2. The Effect of UV-irradiation : (2) P4VPy(4a) bulk solid.

The effect of 260 nm irradiation using Xe-lamp for 10 min on the emission spectra of bulk solid was determined (shown in Fig. 3). Bulk solid had been dried over 140°C and kept in an auto-desiccator. $\lambda_{\max}$ of decrease in the emission intensities were listed in Table 2. Two values of $\lambda_{\max}$ were almost the same. These values of $\lambda_{\max}$ were different from those for the thin film. The intensity of the irradiated light (150 W Xe-lamp, monochromated, at 260 nm) was $0.1 \mu\text{W}/\text{cm}^2$. In Fig. 3a), the initial emission spectrum had three $\lambda_{\max}$ at 300, 400 and 470 nm. As the absorption band around 260 nm (which corresponds to the monomer (Py(1)) band) of bulk P4VPy(4a) was so

large, the emission would be quenched by re-absorption or other mechanisms. After UV-irradiation, the yellowish color appeared only in the surface region. It would be due to the high absorbance of the bulk solid, the irradiation light would not penetrate the lumps of the polymer.

Fig. 3. Changes in emission spectra excited at a) 260 nm and b) 300 nm of bulk solid.

ΔE_m : decrease of emission intensity with irradiation.

Table 2. Decrease in emission intensities of bulk solid.

$\lambda_{\text{ex}}^\dagger / \text{nm}$	$\lambda_{\text{max}}^\ddagger / \text{nm}$
260	400
300	395

$^\dagger\lambda_{\text{ex}}$: the excitation wavelength, $^\ddagger\lambda_{\text{max}}$: the emission maximum wavelength.

3.3. The fast-scanned emission spectra of P4VPy (4a) films with various thickness (No.1 ~ No.4)

3.3.1. The emission spectra of P4VPy (4a) films with various thickness excited at 260 nm

Fig. 4. Emission spectra (excited at 260 nm) of P4VPy(4a) thin films with various thickness.

The emission intensities were determined with fast-scanning (depicted in Fig.4). The emission maximum was slightly shifted from ~ 345 to ~ 355 nm with decreasing the film thickness. The shapes of emission spectra did not significantly change (Fig. 4). Though the emission intensity of No.4 film was very weak, the features of all films were almost all the same to the others.

3.3.2. The emission spectra of P4VPy(4a) films with various thickness excited at 300 nm

The spectra were shown in Fig.5. Only for No.1 and No.2 films, a shoulder around 450 ~ 500 nm region was observed (only slightly for No.2). The emission maxima of all films were ~ 355 nm. While the emission intensity of No.4 film was weak, the shape was roughly same to the others.

Fig. 5. Emission spectra (excited at 300 nm) of P4VPy(4a) thin films with various thickness.

3.3.3. The fast-scanned excitation spectra monitored at 400 nm of P4VPy(4a) films with various thickness

The excitation spectra were measured with fast-scanning (Fig.6). Each excitation spectrum was normalized with the intensity at 250 nm to confirm the ratio of the emission bands. The intensity in $\lambda > 270$ nm region of the excitation spectrum for No.1 film was lower than other films. It would be caused by the high absorbance of film No.1 (Abs. > 1 in 250 ~ 270 nm region).

Fig. 6. Normalized excitation spectra (monitored at 400 nm) of P4VPy(4a) thin films with various thickness.

Table 3. Emission bands of each P4VPy(4a) film.

Sample No.	$\lambda_{ex.}$ / nm
1	250 [†] , 310, 350
2	255, 310, 350
3	260, 350
4	250

[†]The band around 250 nm was quenched.

The spectra had excitation bands at ~250, ~310 and ~350 nm. Each of the emission maximum ($\lambda_{ex.}$) was listed in Table 3. Emission bands appeared differently in each thin film with varied thickness.

3.3.4. The Emission Decay Curves of P4VPy(4a) film No.1

The emission decays were recorded with different filter system. The curves were shown in Fig. 7. In Fig.7a), 320 ~ 600 nm photons were collected. Only UV-region (320 ~ 400 nm) of the photons was determined in Fig.7b). The lifetimes of each emission decay were calculated and listed in Table 4. Curve fitting had done with exponential reconvolutions ($n = 3$).

Table 4. Lifetimes in the emission decay curves of No.1 P4VPy(4a) film excited at 300 nm.

$\lambda_{ex.}$ / nm	Lifetimes / ns	Fig.
320 ~ 600	$>0.1^{\dagger}$, 3.0, 13.7	7a)
320 ~ 400	$>0.1^{\dagger}$, 3.1, 10.3	7b)

[†]The short component would be due to the reflection of the excitation light.

Fig. 7. Emission decay curves of P4VPy(4a) film No.1. a) 320 ~ 600 nm, and b) 320 ~ 400 nm emission

The shortest component in Table 4 could not be the emission from P4VPy(4a) molecules. As the excitation light was filtered with quartz cuvette (with 1cm optical path) containing CuSO₄ solution and color glass filters (the thickness of the filters was < 1 cm), a part of excitation light pulse would be mixed with the emission light. The calculated lifetimes fitted with exponential reconvolutions ($n = 3$) were longer in Fig.7a) than those in Fig.7b).

4. Discussion

4.1. Changes in the absorption spectra of P4VPy(4a) film No.1 with UV-irradiation and subsequent 1 day annealing

With the irradiation at 254 nm using small Hg-lamp for 10 min, the monomer (Py(1)) band decreased and two new absorption bands appeared.

The peaks in longer wavelength around 300 and 400 nm were fitted to ~ 322 and ~ 392 nm, (see Fig. 8). Though the absorption spectrum of P4VPy(**4a**) after 60 min irradiation at 250 nm in P4VPy(**4a**)/Py(**1a**)/H₂O (1:1:0.3 in mol. ratio) system[19] was alike to the irradiated absorption spectrum of P4VPy(**4a**) film No.1, the peak position (356 nm, Abs. ~ 0.3) seemed to be shorter than that in our cases (~ 390 nm in Fig.1).

It had been known that 250 nm irradiation causes the photochemical reaction of Py⁺H(**6**) and / or P4VPy⁺H(**7a**) to form 5-amino-2,4-pentadienal and / or its derivative(**9**; APs, λ_{max} = 339 nm in yellow crystal from acidic solution) (shown in scheme 3)[19,20].

Fig. 8. Fitted peaks in Δ Abs. of P4VPy(**4a**) film No.1 appeared after 10 min irradiation at 254 nm. Peaks were located at 392, 322, 359, 297, and 474 nm in order of decreasing size.

Scheme 3. Ring opening reaction of P4VPy⁺H(**7a**)

They also mentioned that APs(**9**) were unstable and reverted to Py(**1**) residue. The absorption peak in longer wavelength (at ~ 390 nm) of UV-irradiated P4VPy (**4a**) would be rather longer than that of APs(**9**) (for P4VPy(**9a**; AP-P4VPy)) in solid, and the absorption peak in shorter wavelength (at ~ 300 nm) would be longer than the absorption band of P4VPy⁺C₂H₅ (**5aa**)(CF₃SO₃⁻) at 270 nm in aqueous solution.

When the microenvironment of pigment is different, its absorption spectrum is generally considered to be different. Therefore, the possibility could be considered that the spectral change in Δ Abs. (Fig.1b)) was seen on the formation of APs(**9**). Although, the photochemical reactions of forming the yellowish molecules could occur on and near the surface region of the polymeric solids in our cases. The absorption change of P4VPy(**4a**) film No.1 was considered to be reversible, as the absorption changes appeared (Fig.1) returned with subsequent 1 day annealing. With these reasons, the

formation of AP-P4VPy (**9a**) would be doubtful.

Another possibility would be the formation of the charge transfer (CT) band of P4VPy⁺H(**7a**) with some counter ion (the kind of anion is in question). In other groups' cases [11-19], the proton sources were intrinsic or exists inside of the system. The proton source in our cases might be extrinsic, from humid air. It would be necessary to control the humidity around the sample holder during the luminescence measurement. The network, such as P4VPy⁺(**7a**)-H $\cdots$ P4VPy(**8a**), formation would be possible if P4VPy⁺H(**7a**) molecules concurrently exist among the polymer chains. The gel formation reported by Vaganova *et al.* would meet with such crosslink reactions[16-19]. λ_{max} of the CT band of P4VPy⁺R (**5a**) was known to reach to 660 nm in the case of R = C₄H₉ and counter ion : X⁻ = Br⁻[20]. For the elucidation of the photochemical reaction, more detailed studies would be necessary.

The disappearance of the new absorption bands would correspond to P4VPy⁺H(**7a**) changing into the neutral molecule, P4VPy $\cdots$ H(**8a**). H₂O molecule would play an important role in this reaction. Previously We measured N_{1s} and Br_{3p} XPS of P4VPy(**4a**) [1,2] that showed the existence of the plenty of oxygen molecule (up to the same level of nitrogen-atom)[21]. As XPS is measured in $\sim 10^{-5}$ Pa or higher vacuum, the bonding would be so tight and preservation in an auto-desiccator would not be enough for preventing hydrogen-bonding formation.

4.2. Luminescence spectra of bulk solid and film No.1 of P4VPy(**4a**)

4.2.1. Emission spectra of bulk solid and film No.1 of P4VPy(**4a**) excited at 260 nm

Though the emission spectra of bulk and No.1 film were different, it would be due to the re-absorption of the emission or other mechanisms caused by the high absorption of Py(**1**) moieties in P4VPy(**4a**). The spectral change in the emission spectra excited at 260 nm of P4VPy(**4a**) bulk solid would be fundamentally same to that of P4VPy(**4a**) film No.1. Each of the decrease in bulk and No.1 film would correspond to the decrease of the monomer (Py(**1**)) moiety in polymer chain[12-14]. As the shape of the spectra after and before irradiation were almost same and the difference was the intensity only, the spectral change would correspond to protonation from P4VPy(**4a**) to P4VPy⁺H(**7a**) not in the ground-state, but in the excited-state. It may be

natural that P4VPy (**4a**) had low $pK_a(2.50 \sim 3.25)$ in MeOH / H₂O in the ground state[14] and most of Py(**1**) moieties in P4VPy(**4a**) would be neutral. With the change in P4VPy(**4a**) film No.1 with 1 day annealing in an auto-desiccator under dark condition would be the recovery of the monomer (Py(**1**)) band, it would correspond to the increase in the neutral Py(**1**) moiety and to the decrease of some complexes between Py⁺H(**6**) moiety and neighbor molecules.

4.2.2. Emission spectra of bulk solid and film No.1 of P4VPy(**4a**) excited at 300 nm

Though Δ Em. of film No.1 had two peaks at ~ 355 nm and ~ 460 nm with UV-irradiation, only one peak appeared in Δ Em. of bulk solid. The reason for the absence of the longer peak is in question. The shorter peak in Δ Em. of film No.1 would be the monomer band and the similar band could be seen for bulk solid. λ_{max} of decrease was located at ~ 365 nm for film No.1, and at somewhat longer wavelength for bulk solid. It would be also the high absorption of bulk solid (similar to the case of 260 nm excitation). Cáceres *et al.* reported that PVPys(**4**) in dilute solution showed no excimer emission in longer wavelength region than the monomer (Py(**1**)) emission[11-14]. Only Vaganova *et al.* had described that P4VPy(**4a**) had shown the emission band in addition to the monomer (Py(**1**) moiety) emission in viscous solutions or gels[16-20]. The other band in longer wavelength in our cases observed at ~ 460 nm might correspond to the emission band in viscous Py(**1a**) solution (P4VPy(**4a**) / Py(**1a**) (1:1) system) which observed before and after irradiation at 380 nm, and after mechanical perturbation or heating[16], or to that in P4VPy(**4a**) / Py(**1a**) / H₂O (1:1:0.3) system before irradiation at 250nm[19].

In the viewpoint of the concentration of Py(**1**) moiety in polymer solid, the viscous solutions[16] and gels[19] would be the most similar to our cases. The difference from our cases was the irradiation wavelength (380 nm) in ref. 16. In our cases, we did not measure the effect of the longer ($\lambda > 280$ nm) wavelength irradiation, as the irradiation at 366 nm using Hg-lamp for P4VPy(**4a**) bulk solid seemed to take no effect on the color of P4VPy(**4a**). The dependence of the irradiation wavelength would be the subject in future to study the energy levels and molecular state of Py(**1**) moiety in polymeric solids. In addition, the study of the humidity dependence would disclose the properties

of emission bands and would be able to utilize P4VPy(**4a**) for some humidity or UV sensor.

4.2.3. Difference of the excitation wavelength on the emission spectra of P4VPy(**4a**)

The phenomena observed for the bulk solid and the thin film would be almost the same. The difference in spectra might be caused by the high absorption of the bulk solid than that of the thin film. On the other hand, the difference between the phenomena observed for 260 nm irradiation and that observed for 300 nm irradiation would be more essential. The difference between 355 nm and 266 nm excitation were reported in the case of Py(**1a**)-methanol cluster for laser flash photolysis [22]. Hu *et al.* reported that the number of Py(**1a**) in cluster was different at different wavelength excitation[22]. Irradiation light at 300 nm could not be absorbed by the isolated Py(**1**) moieties in the polymeric solids, but could be absorbed by some complexes formed between Py(**1**) moiety and other molecules. Some of the possible complexes were listed below.

<1> (P4VPy)-Py $\cdots$ H-O-H $\cdots$ Py-(P4VPy)
: (i) inter- or (ii) intra-chain hydrogen-bonded complexes
<2> (P4VPy)-P4VPy⁺-H(X⁻) $\cdots$ (P4VPy)
: hydrogen-bonded complexes between ion-pair and hydrogen-bonded with (i) N atom of Py(**1**) moiety or (ii) π -electrons of Py(**1**) moiety
Thus far, the status of the molecules which shows absorption and / or emission in longer wavelength than the monomer (Py(**1**)) absorption and / or emission could not be found out. More detailed experiment would help us to elucidate the structure of these complexes which contained neutral Py(**1**) and / or Py⁺H(**6**) residues, and to distinct between these complexes and quaternized species with spectroscopic detection. All of the emission bands in this study were located in the region $\lambda_{max} < 500$ nm, so those emission bands would not be the same as the emission in the presence of P4VPy⁺R(**5a**)(the emission spectra measured after quaternization)[1-3].

4.2.4. Excitation spectra of bulk solid and film No.1 of P4VPy(**4a**) monitored at 400 nm

The intensity in $\lambda > 270$ nm region of the excitation spectrum for film No.1 would be quenched with the high absorbance of the film (Abs. > 1 at $\lambda < 270$ nm). The excitation band at 310 and 350 nm were seen only for the thick films. These bands would be related to the complexes

discussed in 4.2.3.

Pys(**1**) in P4VPy(**4a**) solids might form some complexes with H₂O molecules adsorbed to the surface of the solid, the neighbor Py(**1**) moieties in the polymer chain, or residual solvent molecules among the polymer chain.

4.3. Emission, excitation spectra and emission decay curves of P4VPy(**4a**) thin films

From Fig.5, the monomer (Py(**1**)) emission would be primal and no other emission band was confirmed. The emission band (shoulder) around ~ 460 nm was observed only for the thick films (No.1 and No.2). As shown in Table 4, the emission in visible (400 ~ 600 nm) region contained longer life time decay component than decay component in the emission in UV region.

5. Conclusions

Comparing with the emission spectra observed after quaternization in our previous reports[1-3] with all emission spectra observed in this study, the emission band around 500 nm observed after quaternization[1-3] would not correspond to some complexes of Py(**1**) moieties in solid P4VPy(**4a**) observed in this study. In other words, the emission band around 500 nm was not seen for any emission spectra of P4VPy(**4a**) without quaternization. More detailed work would be necessary.

Spectral changes observed in this study would be based on extrinsic, outer proton source. The outer proton source (H₂O in air), therefore, would be possible to utilize the photo-induced protonation and deprotonation, as the reaction seemed to be reversible. This might mean the possibility for a new humidity or UV sensor.

The emission band observed in the emission spectra excited at 300 nm would correspond to some complexes of Py(**1**) moieties of P4VPy(**4a**) and neighbor molecules or P4VPy⁺H(**7a**) ($\lambda_{\text{max.}} \sim 370 \text{ nm}$)[12-14]. Classifying the peaks appeared in the luminescence spectra of P4VPy(**4a**) in bulk solids and thin films would be our future work. From the decrease in all emission spectra, the photoproducts of P4VPy(**4a**) would have absorption bands around ~ 300 nm and / or ~ 390 nm, and would not be emissive or would have a lower quantum yield than P4VPy(**4a**).

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