Photochemical Reactions of Poly(vinylpyridines) and its Derivatives in Solid State: Spectral Changes with UV-irradiation and Quaternization

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We had reported the luminescent and photochemical behaviors of poly(4-vinylpyridine) (P4VPy) in solid states. As the emission intensities and spectra are varied with the excitation wavelength, the features of its luminescence properties were difficult to show in usual luminescence spectra. In this study, we introduced “the contour map” to the luminescences of P4VPy and other poly(vinylpyridines)(PVPys) to show their complicated features. PVPys which contain the similar structure to P4VPy show similar behaviors to P4VPy but not the same ones as P4VPy, because of their steric hindrances, hydrophilicities, and other differences in the microenvironment of pyridine rings in these polymeric solids. We also examined the changes in emission contour maps for several bulk solids of PVPys with the photo-induced protonation. The change in the contour maps with the quaternization of thin films of PVPys were determined and discussed.

Keywords: pyridine, pyridinium, polymer surface protonation, quaternization, luminescence

1. Introduction

Pyridines (1: Pys, for example, pyridine (1a) (Py)) are known to be quaternized to hydrocarbon substituted pyridiniums (2: Py'R) (see Scheme 1) with various compounds such as halogenated hydrocarbons (3)[1].

![Pyridine and Pyridinium Structures](image1)

Scheme 1. Quaternization of Py (1a)

They are also known as low fluorescence quantum yield compounds[2-5]. The first report of Pys(1) fluorescence was in 1977[2]. The fluorescence quantum yield of Pys(1) was varied with the excitation wavelength as it has plural absorption bands in close region. The yield for \( \pi-\pi^* \) excitation was higher than that for \( \pi-\pi^* \) excitation. Polymeric compounds such as poly(4-vinylpyridine)(P4VPy)(4a) and other poly(vinylpyridines)(PVPys)(4) were also quaternized as pyridine derivatives. They are often quaternized with halogenated hydrocarbons(3)[6] to change polymer solubility, viscosity and other properties.

![Quaternization Reactions](image2)

Scheme 2. Quaternization of P4VPy (4a)

(\( x \): the extent of quaternization)

In previous studies, we reported the luminescence properties of P4VPy(4a) thin films [7-10]. With quaternization, the maximum emission wavelength excited at 300 nm was redshifted more than 100 nm[7,8]. On the other hand, previously reported for P4VPy(4a) solutions [21-24], with even a few min-irradiation at 254/260 nm, the absorption and emission spectra were found to change[10]. Recently, to avoid the
absorption and emission change with UV-irradiation, we decided to employ fast scanning (1200 nm/min or faster) rate[10]. It seemed to be important to distinguish the quaternization including hydrocarbon-substitution from protonation. In this study, we introduce "emission contour map" to show the emission properties of PVPys(4). With this new tool for us, the difference between the quaternization and protonation would appear in the maps.

2. Experimental
2.1. Materials and Sample preparation
For thin film samples, P4VPy(4a) (Sigma-Aldrich Co., 47,234-4 Mw ~ 60,000) and poly(2-vinylpyridine)(P2VPy)(4b) (Sigma-Aldrich Co., 52,332-1, Mw ~ 37,500) were used after reprecipitation from methanol to diethyl ether and drying over 140 °C. For bulk samples, P4VPy (4a) and P2VPy (4b) were used as received. Other PVPys, Ethyl bromide(3a) (EtBr) (98.0%, Kanto Chemicals Co., Inc.) and cyclopentyl bromide(3b)(c-PrBr) (Tokyo Kasei Kogyo Co., Ltd.) were used without further purification. UV spectral grade methanol (Dojindo Molecular Technologies, Inc.) and HPLC grade diethyl ether (Wako Pure Chemical Industries, Ltd.) were used as supplied. The synthetic quartz plates (10 × 45 × ~1 mm²) are used after cleaning. The same samples were spin-coated as previously reported method[7-10] and then dried over 150 °C for about 1 h under deaerated condition. Details of PVPys(4) were as follows. Cross-linked P4VPy(4c) (P4VPy-CL)(Sigma-Aldrich Co., 22,696-3, 2% cross-linked), poly(4-vinylpyridine-co-styrene)(4d) (P4VPy-St)) (Sigma-Aldrich Co., S43,637-2), poly(2-vinylpyridine-co-styrene)(4e)(P2VPy-St)) (Sigma-Aldrich Co., 18,460-8, Mw ~ 220,000), 2,6-Di-tert-butylpyridine polymer-bound(4f) (P(4VPy-Bu2)) (Sigma-Aldrich Co., particle size 200-400 mesh, loading:~1.8mmol/g, 1% cross-linked with divinylbenzene, 37,782-1) and poly(4-vinylpyridine-co-butyl methacrylate)(4g) (P(4VPy-BMA)) (Sigma-Aldrich Co., 30,625-8, beads: 300 ~ 1000 μm, water: 55 wt.%) were used as supplied.

2.2. UV-irradiation Process
A 10 W small mercury lamp was employed. A film sample or a bulk sample in a cylindrical sample holder with quartz window was irradiated at 254/365 nm from ~1 cm distance.

2.3. Quaternization Process
Inside the closed glass dishes, PVPy(4) spin-coated films and a small bowl of liquid EtBr(3a) or c-PrBr(3b) were placed as shown in Fig.1. The space in glass dishes was filled with the vapor of EtBr(3a) or c-PrBr(3b) during quaternization.

Figure 1. Setup for the quaternization processes.

2.4. Luminescence measurements of PVPys(4) films.
As described before[6-9], absorption spectra were measured with a double beam UV-3200 UV-visible spectrophotometer, (Hitachi). For luminescence spectra, an F-4500 fluorescence spectrophotometer (Hitachi) with options for solid samples was used. As PVPys(4) showed strong diffraction and reflection, it was very difficult to elucidate the diffraction excitation light. Each contour map was made with sequential scans of emission spectrum varying excitation wavelength. 2 or more straight-lines across the map correspond to diffraction excitation light.

3. Results and Discussion
3.1. UV-visible Absorption Spectra of PVPys(4)
Maximum Absorbance of thin films of P4VPy (4a) and P2VPy(4b) were ~3 and >4, respectively. Absorbance of other bulk samples PVPys(4) did not determined as they had higher absorbance than film samples.

3.2. Luminescence of PVPy(4) and PVPy'R(5) films.
Luminescence of P4VPy(4a) and P2VPy(4b) were determined before and after quaternization.
3.2.1. Emission Contour Maps of P4VPy(4a) and P2VPy(4b) thin films
Luminescence of spin-coated P4VPy(4a) and P2VPy(4b) films were recorded (see Figs. 2a and 2b), respectively. We use the expression Em(λexc, λem) for the maximum or center excitation and emission wavelength of each emission bands, hereafter. In the bottom part of both contour maps, similar strong emissions Em(≤260,280-650) distributed widely in the region of 280nm ≤ λem ≤ 650 nm correspond to the excitation wavelength region of λexc ≤ 260 nm, containing high intensity diffraction were observed. It would correspond to the emission from π-π* excitation[2,3,11-15] and emission from protonated molecule[11-25]. For
P4VPy(4a), in 260 nm ≤ λex ≤ 285 nm, two separated-component emissions, Em(264,328) in 300nm≤λem≤420nm and Em(272,502) in 420nm ≤ λem ≤ 600 nm, from n–π* excitation[2-5] and protonated molecule[11-25], were observed.

In the map of P4VPy'c-PrBr'(5ab)(Fig. 3c), a strong emission band, Em(442,556) in visible region appeared and in the map of P4VPy'EtBr' (5aa)(Fig. 3a)), a very weak emission band, Em (455,496) was seen in visible region. It could be from some charge-transfer (CT) complex[26].

For P2VPy(4b), in 270 nm ≤ λex ≤ 300 nm, two separated-component emissions, Em (284,368) in 310nm≤λem≤430nm and Em(272, 502) in 420nm ≤ λem ≤ 600 nm, from n–π* excitation [2-5] and protonated molecule[11-25], were observed. Longest parts of both PVPys(4a,4b) emissions were longer than the cases in previous reports of other systems [2-6,11-25]. For P4VPy(4a), a weak emission, Em(>312,>358) was observed.

3.2.2. Changes in Emission Contour Maps of P4VPy(4a) and P2VPy(4b) thin films with quaternization using EtBr(3a) and c-PrBr(3b).

The emission contour maps were shown in Fig. 3 and peaks were listed in Table 1.

<table>
<thead>
<tr>
<th>PVPy'RB'R</th>
<th>Em(λex, λem)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5aa</td>
<td>(296,490)(364,406)(456,496) w(455,496)</td>
</tr>
<tr>
<td>5ba</td>
<td>(≥235,358)(284,502)(288,370) w(472,508)</td>
</tr>
<tr>
<td>5ab</td>
<td>(263,556)(442,556)</td>
</tr>
<tr>
<td>5bb</td>
<td>(291,370) w(281,514)</td>
</tr>
</tbody>
</table>

1Weak emissions were marked as “w”.

From Figs. 3a)–3d), each contour maps of PVPy'R (5) was changed and new emission appeared in longer visible region. For P2VPy'c-PrBr(5bb), longer emission was very weak. It would be the low reactivity of c-PrBr(3b) between P2VPy(4b).

3.3. Emission Contour Maps of bulk P4VPys(4)

3.3.1. Emission Contour Maps of P4VPy(4a) before and after UV-irradiation at 254/365 nm.

The emission contour maps were shown in Figs. (4a)–4c) and peaks were listed in Table 2. Before irradiation, emission peaks were seen as two separated bands below and above the level of
The lower emission band of \( \lambda_{ex} \leq 275 \text{ nm} \) was similar to that of P4VPy(4a) thin film. In the upper part (\( \lambda_{ex} \geq 275 \text{ nm} \)) of the contour map, three bands were seen. The lowest one, Em(296,340) would correspond to the weak band of P4VPy(4a) thin films Em(\( \geq 312,358 \)). The middle one, Em(364,412) was also seen for P4VPy'EtBr(5aa)(Fig. 3c)) and for P4VPy(4a) thick spin-coated films (data not shown). This band was also seen for various derivatives of PVPys(4). Though the emission characteristics had never revealed yet, it could be related to hydrogen-bonding complex (discussed in 3.3.3.) between pyridine rings and solvents or H2O residue[11-25].

\[ \text{Figure 4. Emission Contour Maps of P4VPy(4a) bulk solid. a) before irradiation, b) after 5min 254 nm irradiation, and c) after successive 20 min 365 nm irradiation.} \]

<table>
<thead>
<tr>
<th>Table 2. Peaks in the Maps of P4VPy (4a) bulk solid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{Em}(\lambda_{ex}, \lambda_{em}) ]</td>
</tr>
<tr>
<td>before ( (364, 412)(&gt;458, &gt;475) ) w(296, 340)(^2)</td>
</tr>
<tr>
<td>254 nm irrad. ( (&gt;458, &gt;474) ) w(296, 340)(^2)</td>
</tr>
<tr>
<td>365 nm irrad. ( (&gt;453, &gt;474) ) w(300, 340)(^2)</td>
</tr>
</tbody>
</table>

\(^2\)Weak emissions were marked as "w".

\[ \text{Figure 5. Emission Contour Maps of P2VPy(5) bulk solid. a) before irradiation, b) after 145min 254 nm irradiation, and c) after successive 40 min 365 nm irradiation.} \]

<table>
<thead>
<tr>
<th>Table 3. Peaks in the Maps of P2VPy (4b) bulk solid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \text{Em}(\lambda_{ex}, \lambda_{em}) ]</td>
</tr>
<tr>
<td>Before ( (304,346)(^2)</td>
</tr>
<tr>
<td>254 nm irrad. ( (324,370) ) w(( &gt;479, &lt;518 ))(^2)</td>
</tr>
<tr>
<td>365 nm irrad. ( (316,518) ) w(( &gt;459, &lt;497 ))(^2)</td>
</tr>
</tbody>
</table>

\(^2\)Weak emissions were marked as "w".

3.3.2. Emission Contour Maps of P2VPy(4b) before and after UV-irradiation at 254/365 nm

The changes in emission contour maps were shown in Figs. 5a)–5c) and peaks were listed in Table 3. Irradiation at 254 nm caused smaller effect on the emission contour map. It would due to the steric hindrance.

\[ \text{Formula 1. Structures of P4VPy-cl(4c), P(4VPy-co-St) (4d) and P(2VPy-co-St)(4e).} \]

3.3.3. Emission Contour Maps of P4VPy-cl(4c) before and after UV-irradiation at 254/365 nm.
The emission contour map of P4VPy-cl (4c) was different from linear P4VPy (4a) and similar to P2VPy (4b). The obtained maps were shown in Figs. 6a–6c and peaks were listed in Table 4.

![Emission Contour Maps of P4VPy-cl(4c) bulk solid. a) before irradiation, b) after 5 min 254 nm irradiation, and c) after successive 20 min 366 nm irradiation.](image)

**Figure 6.** Emission Contour Maps of P4VPy-cl(4c) bulk solid. a) before irradiation, b) after 5 min 254 nm irradiation, and c) after successive 20 min 366 nm irradiation.

**Table 4.** Peaks in the maps of P4VPy-cl(4c).

<table>
<thead>
<tr>
<th>Before</th>
<th>(320, 370) w(412,454)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>254 nm irrad.</td>
<td>(320, 448)</td>
</tr>
<tr>
<td>365 nm irrad.</td>
<td>(320, 364)</td>
</tr>
</tbody>
</table>

²Weak emissions were marked as “w”.

Comparing with the cases of previous studies of UV-irradiation on P4VPy(4a)[21-24], though they show strong diffraction to be an obstacle to detect emission peaks in the emission contour maps, both P4VPy(4a) and P4VPy-cl(4c) showed an obscure but similar emission band in visible region after 254 nm irradiation. P4VPy-cl(4c) chains would be sterically hindered and be prevented to form hydrogen bonds around Py(1)-rings before irradiation. With 254 nm irradiation, pyrimidinium ion would be formed. As Py(1a) is known to form protonated-Py (Py⁺H⁻) (6) with UV-irradiation because of the difference between pKa and pKₐ⁺. Protonation behaviors of PVPys (4) were also reported [11-25].

For example, in P4VPy(4a) emission contour maps, increase of Em(>458,<474) with 254 nm irradiation would correspond to the formation of protonated-pyridine(7a) (P4VPy⁺H⁻), and decrease of Em(364,412) would correspond to decrease of hydrogen-bonded pyridine(8a) (P4VPy⁺H⁻).

![Emission Contour Maps of P(4VPy-St)(4d) bulk solid. a) before irradiation, b) after 5 min 254 nm irradiation, and c) after successive 20 min 365 nm irradiation.](image)

**Figure 7.** Emission Contour Maps of P(4VPy-St)(4d) bulk solid. a) before irradiation, b) after 5 min 254 nm irradiation, and c) after successive 20 min 365 nm irradiation.

3.3.4. Emission Contour Maps of copolymers, P(4VPy-St)(4d) and P(2VPy-St)(4e) before and after UV-irradiation at 254/365 nm.

Emission contour maps were shown in Figs. 7a–7c and 8a–8c). For P(4VPy-St)(4d), only one peak, Em(372,428) was seen in Fig.7a) and it was decreased with 254 nm irradiation (Fig.7b)). A new peak, Em(472,515) appeared in Fig.7b). It would be same emission reported in the case of P4VPy(4a)/Py(1a)/H₂O[21] after UV-irradiation. Though P(4VPy-St)(4d) was 90 : 10 (block) copolymer, no other peak which corresponded to PST was not obviously seen. Em(372,418) would correspond to P4VPy·H(8a) as it decreased with
254 nm irradiation. On the other hand, Em(472, 515) in Fig.7b) would due to P4VPy-H\(^+\)(7a). In Figs. 8a), 8b), no significant change was observed. It seemed to be a common feature of P2VPy(4).

![Formulae 2. Structures of the Py-H(6), P4VPy-H(7a) and P4VPy-H(8a) (x: the extent of protonation)](image)

Each map was shown in Figs. 10a)~10c), respectively. Peaks in Figs. 10a)~10c) were listed in Table 5.

![Figure 8. Emission Contour Maps of P(2VPy-St)(4e) bulk solid. a) before and b) after 30min 254 nm irradiation.](image)

Figure 9. Emission Contour Maps of P(4VPyBu2)(4f) bulk solid. a) before and b) after 30min 254 nm irradiation.

![Figure 10. Emission Contour Maps of P(4VPy-BMA)(4g) bulk solid. a) before irradiation, b) after 30 min 254 nm irradiation, and c) after successive 20 min 365 nm irradiation.](image)

3.3.5. Emission Contour Maps of P(4VPyBu2) (4f) before and after UV-irradiation at 254/365 nm.

A highly bulky, sterically hindered derivative, P(4VPyBu2) (4f) was examined for UV-induced change. No significant change was seen in visible region in the emission contour maps. Only one peak, Em(320,376) was observed. In UV-excited emission range, short wavelength part decreased at 254 nm irradiation.

3.3.6. Emission Contour Maps of P(4VPy-BMA) (4g) before and after UV-irradiation at 254/365 nm.
They resemble to those of P4(4VPy-St)(4d) in Figs. 7a–7c). Due to the cation-binding characteristics of butyl methacrylate moiety and high water content (55%), ionic complex between P4VPy'H(8a) and OH of H2O would easily form and remain in solid. In cases of P(4VPy-St)(4e), P(4VPy-BMA)(4g) and P4VPy(4a), longer wavelength-band appeared in visible region with 254 nm irradiation, and they could be some ionic complex formed between P4VPy'H(8a) and other aromatic rings (pyridine or phenyl) or butyl methacrylate moiety. From results of P(4VPy-BMA)(4g), pKa of the polymeric solids would be too high to keep ionic complex in solid for long.

Table 5. Peaks in the maps of P(4VPy-co-BMA)(4g).

<table>
<thead>
<tr>
<th>Em(λex,λem) before</th>
<th>254 nm irradi.</th>
<th>365 nm irradi.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(368, 436)</td>
<td>(372, 430)</td>
</tr>
<tr>
<td></td>
<td>w(472, 515)²</td>
<td>w(456, 502)²</td>
</tr>
</tbody>
</table>

²Weak emissions were marked as “w”.

3.3.7. Emission Contour Maps of P(4VPy-co-4VPy'MeCl)(4h) before and after UV-irradiation at 254/365 nm.

Changes in the emission contour maps were shown in Figs. 11a–11c). Peaks were summarized in Table 6. Two peaks were seen in Fig. 11a). One of them, Em(380, 448) was influenced by the UV-irradiation at 254 nm. As this peak was decreased with irradiation, Em (380, 448) would be some hydrogen-bonded complex. Contrary to Em(324, 428), Em(380, 448) would come from Py'MeCl. Though it seemed to be shorter than PVPy'RB in our previous reports[7, 8], P4VPy'EtBr(5aa) and P4VPy'c-PrBr(5ab) in this study, it was not strange comparing CT degree[26] of Br' with that of Cl'.

Table 6. Peaks in the Maps of P(4VPy-co-4VPy'MeCl) (4b) bulk solid.

<table>
<thead>
<tr>
<th>Em(λex,λem) before</th>
<th>254 nm irradi.</th>
<th>365 nm irradi.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(324, 418)</td>
<td>(328, 436)</td>
</tr>
<tr>
<td></td>
<td>(380, 448)</td>
<td>(324, 430)</td>
</tr>
</tbody>
</table>

²Weak emissions were marked as “w”.


All bulk PVPys(4) but P2VPy(4b) showed distinct emission bands in visible region. This visible emission would correspond to that from some excited hydrogen-bonded complex, similar to the emission reported for acidic solutions of PVPys (4)[11-20, 25] and P4VPy(4a) gel systems[21-24]. Contrary to P4VPy(4a), P(4VPyBu) (4f) and other substituted PVPys(4) showed no significant change in visible region with 254 nm irradiation, because of their steric hindrance. For several kinds of P4VPys(4a, 4c, 4d, (4g), 4h), a decrease around 385 nm was seen with 254 nm irradiation. In the maps for copolymer or cross-linked samples, emission from phenyl or butyl methacrylate could not distinguish from that from Py(1) moieties. For the ionic species, P(4VPy-co-4VPy'MeCl) (4b) showed two visible bands before irradiation.

4. Conclusions

We introduced the emission contour map for luminescence measurements of solid PVPys(4), as the emission properties of PVPys(4) are highly excitation wavelength-dependent. As n-π* and π-π* absorption bands of Pys(1) are located nearby, it was difficult to distinguish between them. From the maps of P4VPy(4a) and P2VPy(4b) thin films, emissions excited at λex < 300 nm was found to contain both n-π* and π-π* excitations and they

Figure 11. Emission Contour Maps of P(4VPy-co-4VPy'MeCl)(4h). a) before irradiation, b) after 30 min 254 nm irradiation, and c) after successive 20 min 365 nm irradiation.
separated at $\lambda_{ex} \sim 260$ nm. And the emissions excited at $\lambda_{ex} \geq 300$ nm was found to be different from monomer emission bands from the maps of PVPs(4). Though the nature of this emission band had not revealed yet, it would become evident with detailed investigation. It would be possible that the visible emission bands have some relationships with hydrogen bondings and CT interactions between Py(1) rings and other molecules, such as phenyl rings, other pyridine rings, water and other solvent molecules.

The effect of 254 nm ($\pi$-$\pi^*$ absorption) irradiation was seemed to decrease the hydrogen-bonded molecules and increase the ionic complex in the polymeric solids. This wavelength would correspond to the hydrogen-bonded complex of P4VPy(4a) which was reported by Piérola et al. [15]. Though the effect of 365 nm was not so clear, the increased emissions caused with 254 nm irradiation seemed to decrease in most cases.

In the cases of quaternization, new bands appeared in Figs. 3a)–3d) (in Fig.3d), the intensity was very low) of UV-excited emission would correspond to the pyridinium emission from pyridinium $\pi$-$\pi^*$ excitation. Contrary to it, the new band seen in only Figs. 3a) and 3c) (in Fig. 3c), very week) of vis-excited emission was seen to be the emission from CT complex. These results were different from the UV-induced protonation of PVPs(4).

With more detailed investigations, the nature of the absorption and emission bands for neutral, cationic and hydrogen-bonded pyridine derivatives would appear.

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References