Spectroscopic Properties and UV-irradiation Effects on the Complexes formed between Poly(vinylpyridines) and Polymeric Hydrogen-Bond Donors

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We made complexes between poly(vinylpyridine) (PVPy) and poly(hydroxyethyl methacrylic acid) (PHEMA), or between PVPy and poly(4-vinylphenol) (PVPhOH). Complexes containing PVPhOH were colored simultaneously with mixing, contrary to those containing PHEMA. Poly(2-vinylpyridine) and PHEMA formed clear solution, though poly(4-vinylpyridine) formed cloud one, and it could come from the difference of ionization of PVPys. PHEMA only formed precipitations with PVPy-polystyrene copolymers, and it could be caused by the interference of benzene ring to hydrogen-bonds among pyridine rings. Contrary to PHEMA complexes, 2D emission spectra of PVPhOH complexes showed no significant change with UV-irradiation at 254 nm.

Keywords: poly(vinylpyridine), hydrogen-bonded complex, UV-irradiation effect, poly(4-vinylphenol), poly(hydroxyethyl methacrylate)

1. Introduction

1.1. Studies on photo-excited states of pyridines.

Photophysical and photochemical properties of pyridine derivatives (Pys; **1**) [for example, 1-5] and pyridinium derivatives (Py⁺Rs; **2**) [for example, 6-8] had been investigated in '70s and earlier. In these days, reconsidered using the fast equipments for the ultrafast phenomena [for example, 9-12]. Pys(**1**) are easily protonated in their photo-excited states. Schematic representation of the speculated photochemical process of free pyridine (Py; **1a**) can be described as follows.

Scheme 1. Photoinduced-processes of Py(**1a**)

Photophysical and photochemical properties of

polymeric derivatives had also been investigated [16-31]. Among poly(vinylpyridines) (PVPys; **3**), poly(2-vinylpyridine) (P2VPy; **3a**) and poly(4-vinylpyridine) (P4VPy; **3b**) are the most frequently studied species. P2VPy(**3b**) was reported by Piérola *et al.* to be protonated with UV-irradiation (UV-irrad.) [13].

Complex formation between Pys(**1**) including PVPys(**3**) and H⁺ or H-bond donors had also been reported [32-37]. PVPys(**3**) was found to form ionic complex between polymeric acids [33-36].

1.2. Our previous reports on Pys(**1**) and PVPys(**3**)

We have investigated the quaternization and UV-irrad. effects on PVPys(**3**), especially, P2VPy (**3a**) and P4VPy(**3b**) [38-50]. With UV-vis or IR spectroscopic measurements, we had never found the proof of protonated PVPys(**3**) in the solid states. But we found some interesting phenomena and properties of PVPys(**3**). For example, differences of the UV-irrad. effects on luminescence [43,44,46, 48] and surface morphologies of them [48,50].

We introduced 2D emission spectrum (Excitation Emission Matrix; EEM) [51,52] to classify the

emission bands of PVPys(3) [42-48,50]. Furthermore, we also determined EEMs and long lifetime emission decays (from 1 ms to 1 s range) of Pys(1) and PVPys(3) at 77 K[46]. The result of 1,4-dimethylpyridinium *p*-toluenesulfonate (DMP; 1b) showed that the emission band of $\lambda_{em} \sim 550$ nm could be derived from a complex between positively charged Py-ring and some negatively charged aromatic ring (including Py-ring). The ionic pair in PVPys(3), especially UV-irradiated PVPys(3) might not be the distinct pyridinium, as the charge on N atom in Py-ring of PVPys(3) appeared to be smaller than +1 in N1s XPS spectra [49]. As a matter of course, XPS spectra were recorded under high vacuum ($\sim 10^{-8} \sim 10^{-9}$ Pa), the state of water or MeOH residue in the very surface region of polymeric solid would be different from that under air conditions. In addition, from the change of O1s spectra according to UV-irrad., water and O₂ molecule is conjectured to be introduced in the surface region of polymeric films from the atmosphere[49]. Many interesting phenomena have been found but the mechanisms of the photo-irradiation processes are still in question.

1.2. Classification emission bands of PVPys(3)

Table 1. Emission bands of PVPys(3)

Emission bands	Speculated classification of each emission band
A	monomer emission ($\pi\text{-}\pi^*$ excitation) of pyridine-rings
B	monomer emission ($n\text{-}\pi^*$ excitation) of pyridine rings
B ⁺	or protonated / quaternized ionic species
C	CT-like-emission from higher excited states
D	emission from hydrogen-bonded species
	emission from CT-complexes formed in the ground state

[†]Bands B and -B⁺ are excited at same λ_{ex} .

In EEMs, almost all emission bands appear between two Releigh scattering lines (they appear at λ_{ex} and $2 \times \lambda_{ex}$). Emission bands in luminescence of PVPys(3) were classified into four emission bands, A ~ D (listed in Table 1 and Fig. 1). Band-A corresponds to $S_0 \rightarrow S_2$ transition ($\pi\text{-}\pi^*$) of Py-ring and its excitation wavelength (λ_{ex}) ≥ 270 nm. In this region, absorbance of the spin-coated thin films of PVPys(3) is over 3, so band-A is not possible to analyze in detail with fluorescence spectroscopy. Band-B corresponds to $S_0 \rightarrow S_1$ transition ($n\text{-}\pi^*$) of Py-ring, protonated-Py or hydrogen-bonded Py (these three states are drawn in the lower part of Scheme 2) and $\lambda_{ex} \leq 270$ nm.

Figure 1. Schematic representation of the speculated classification of emission bands in EEMs for PVPys(3) (vertical axis : excitation wavelength (λ_{ex}), horizontal axis : emission wavelength (λ_{em}))

If the sample is quaternized, free quaternized-Py also appears in this region. As these absorption bands are too close and the features of them resemble each other to distinguish, it is difficult to assign them by absorption spectra.

1.3. Polymer complexes made of PVPys(3) and H-bond donors

In one of our previous study, we reported luminescence of the complex between PVPys(3) and poly(acrylic acid)(PAA; 4). Hereafter, we use abbreviation A+B for the complex made of A and B. In each mixture of the methanolic solution of PVPy(3) and PAA(4), white precipitate was formed immediately after mixing of two polymer solutions [43]. So we reported only about the luminescence of bulk precipitates or supernatants of the formed complexes. We examined complex between P2VPy(3a), P4VPy(3b), poly(2-vinyl-pyridine-co-styrene)(P2VPy-St; 3c), or poly(4-vinylpyridine-co-styrene)(P4VPy-St; 3d), and PAA(4). Rough tendency of luminescence of all complexes were similar. Band-B emission was seen for P2VPy(3a)+PAA(4), P4VPy(3b)+PAA(4), P2VPy-St(3c)+PAA(4) and P4VPy-St(3d)+PAA(4), on the other hand, band-C was seen only for P4VPy(3b)+PAA(4) and P4VPy-St(3d)+PAA(4). It should be caused by the difference of steric hindrance around the N atom of Py-ring.

Degrees of UV-effect also depend on the N atom position of Py-ring. Band-D appears after UV-irrad. at 254 nm for all samples. The ratio of (band-D / band-B or band-C) was (P2VPy(3a)+PAA(4)) $\geq$ (P4VPy(3b)+PAA(4)) $\geq$ (P2VPy-St(3c)+PAA(4)) $\geq$ (P4VPy-St(3d)+PAA(4)). The reason of the above ratio (P4VPys samples) $\geq$ (P2VPys samples) could come from the degree of ionic species (in N1s XPS spectra, the ratio of ionic nitrogen to all Py-ring in P2VPy(3a)+PAA(4) was almost twice of that in P4VPy(3b)+PAA(4)) in those complexes as Zhou *et al.* reported [34]. The

effect of copolymerization was seen mainly for the stabilization of the long wavelength bands, band-C and band-D. Those emission bands disappeared faster in EEMs of copolymers (with polystyrene) than in those of PVPy homopolymers(**3a** and **3b**).

We also made complexes between PVPys(**3**) and poly(hydroxyethyl methacrylic acid)(PHEMA; **5**) or poly(4-vinylphenol) (PVPhOH; **6**), the EEMs of those complexes made with PVPy(**3**)+PHEMA(**5**) and PVPy(**3**)+PVPhOH(**6**) showed intense scattering and obscure emission bands, except for P2VPy(**3a**)+PHEMA(**6**)[53]. Contrary to P4VPy(**3b**)+PHEMA(**6**), P2VPy(**3a**)+PHEMA(**6**) formed a clear solution[53]. We report the luminescent properties of these complexes in this paper.

Scheme 2. Chemical structures of PVPys(**3**), H-bond donors (PAA(**4**), PHEMA(**5**), PVPhOH(**6**)) and each state of Py-ring.

2. Experimental

2.1. Materials and sample preparation

P2VPy(**3a**), P4VPy(**3b**) were purchased from Sigma-Aldrich Japan K.K. and were used after reprecipitation from MeOH to diethyl ether. All other polymers, P2VPy-St(**3c**), P4VPy-St(**3d**), PAA(**4**), PHEMA(**5**), and PVPhOH(**6**) were also purchased from Sigma-Aldrich Japan K.K. and used as supplied. MeOH was of fluorescence grade.

2.2. UV-irradiation and Luminescence measurements

All samples were irradiated at 254 nm with a filtered mercury lamp (10W). Fluorescence spectra and EEMs were recorded with a Hitachi F-4500 Fluorescence spectrophotometer. We use the expression $Em(\lambda_{ex}, \lambda_{em})$ for the maximum or center excitation and emission wavelength of each emission bands. Because of the strong scattering of polymer surfaces, the maximum or center of the emission band was often difficult to discriminate. The wavelengths of weak emission bands are subject to shift. Usually λ_{ex} is varied in the range of 220 ~ 550 or 600 nm and λ_{em} is 220 ~ 650 or 700 nm.

3. Results and Discussion

3.1. Polymer complex formation between PVPys(**3**) and PHEMA(**5**)

As described in 1.3., complexes were made with PVPys(**3**) and polymeric H-bond donors and were determined. The appearance of all kinds of

complexes are shown in Table 2, and emission bands in each EEM of PVPys(**3**) or PVPys(**3**)+PVPhOH(**6**) is listed in Table 3 (next page).

Table 2. Appearances of PVPys(**3**)+H-bond donors

before →after [†]	P2VPy(3a) P2VPy-St(3c)	P4VPy(3b) P4VPy-St(3d)
PAA(4)	P [‡] : white → yellow + reddish S [‡] : clear → slightly yellow	P: white → yellow S: white → yellow
	P: pale yellow → deep yellow S: white → deep yellow	P: slightly yellow → yellow S: clear → yellow
PHEMA (5)	S: clear → yellow S: white cloud → deep yellow	upper S: white lower S: white → pale yellow P: white → pale yellow S: white → slightly yellow
	P: pale brown S: slightly yellow → yellow	P: pale yellow S: slightly yellow → reddish brown
	P: pale brown S: slightly brown → yellow	P: pale yellow S: slightly yellow → yellowish brown
PVPhOH (6)		

[‡] P: precipitate, S: solution.

[†] before → after: appearance before UV-irrad.

→ appearance after UV-irrad.

3.2. Luminescence of P2VPy(**3a**)+PHEMA(**5**) and P2VPy-St(**3c**)+PHEMA(**5**)

Figure 2. EEMs of: P2VPy(**3a**)+PHEMA(**5**)((a),(b)) and P2VPy-St(**3c**)+PHEMA(**5**)((c),(d)).

Left: before UV-irrad., right: after 30 min UV-irrad.

Among of all polymer complexes, only the P2VPy(**3**)+PHEMA(**5**) complex didn't show the phase

separation. In particular, P2VPy(**3a**) formed clear solution with PHEMA(**5**).

Table 3. Appearances of PVPys(**3**)+H-bond donors

before →after [†]	P2VPy(3a) P2VPy-St(3c)	P4VPy(3b) P4VPy-St(3d)
PHEMA (5)	S:(232,328)	upper S: (228,334)
	(300,322)(332,364)	(296,322)(296,334)
	(412,466) →	(368,412)→(228,322)
	(228,352)(264,346)	(296,322)(296,334)
	(296,346)	(368,412)(442,463)
	(344,400)	lower S:(296,322)
	(424,448)(472,526)	(296,334)(372,412)→
	(550,570) [§]	(228,352)(232,406)
		(296,322)(296,334)
		(372,412)(430,474)
PVPPhOH (6)		P:(296,315)
	S:(298,324)	(340,406)(356,418)→
	(302,357)(344,412)	(300,406)(356,418)
	(392,415) →	(455,480)
	(240,390)	S:(236,304)
	(244,340)(280,340)	(292,316)(303,380)
	(296,324)(296,526)	(352,424)(390,490)→
	(300,448)(425,445)	(236,304)(296,322)
	(484,526)	(328,418)(390,480)
	P:(332,376)	P: (232,388)
	(404,454)(448,490)→	(370,395)(425,450)
	(336,382)(400,454)	(459,502)(469,513)
	(452,496)(476,510)	→(365,390)(404,448)
		(452,496)(472,514)
	S:(232,304)	S:(232,304)
	(280,304)(368,430)	(280,310)(304,334)
	(560,592) →	(456,586)(570,595)
	(232,304)(280,304)	→(232,304)(280,307)
	(376,448)(560,598)	(304,329)(445,460)
		(556,592)
	P: (332,388)	P:(224,394)
	(376,424)(452,496)	(375,395)(470,500)
	(475,514)→(280,328)	(384,412)(472,514)→
	(332,388)(392,448)	(248,388)(368,396)
	(448,490)(474,514)	(388,442)(368,502)
		(467,502)
	S:(232,305)	S:(232,304)
	(284,303)(304,334)→	(260,304)(280,310)
	(224,304)(240,304)	(308,334)(322,358)
	(280,304)(300,328)	(370,430)(444,586)
	(394,496)(569,593)	(570,595)→(232,304)
		(256,304)(280,310)
		(304,328)(400,436)
		(528,592)(570,595)

[†] P: precipitate, S: solution, and [†]appearance before UV-irrad. → appearance after UV-irrad.

[§] Weak bands are underlined, and weak bands near strong scattering / strong emission band are meshed.

Though no color or precipitate was appeared, the viscosity of the mixture solution was found to be high, and the EEM of the complex was different from P2VPy(**3a**) and showed the UV-irrad. effect (shown in Fig. 2). Complex of P2VPy-St(**3c**)+PHEMA(**5**) formed white cloudy solution. In the EEM of the above complex before UV-irrad., band-B and another one, band-C or band-D (D_1 in Fig. 1) were seen. Similar to those of P2VPy(**3a**)+PHEMA(**5**), two band-D (D_1 and D_2 in Fig. 1) could be seen. Except for the slight appearance of an intermediate wavelength emission band for the unirradiated complex of P2VPy-St(**3c**), the feature of both P2VPys(**3a,3c**) were similar.

3.3. Luminescence of P4VPy(**3b**)+PHEMA(**5**) and P4VPy-St(**3d**)+PHEMA(**5**)

Figure 3. EEMs of P4VPy(**3b**)+PHEMA(**5**)(lower solution) and P4VPy-St(**3d**)+PHEMA(**5**)(upper solution). Left: before and right: after 30 min UV-irrad.

In both phases of P4VPy(**3b**)+PHEMA(**5**) and in lower solid of P4VPy-St(**3d**)+PHEMA(**5**), band-C appeared mainly. In P4VPy(**3b**)+PHEMA (**5**)'s EEMs, both phases showed similar EEMs and band-B also appeared in both phases. With 30-min-UV-irrad, only a slight shoulder of band-D was seen (as shown in Fig. 3a) and 3b)). In the solid phase of P4VPy-St(**3d**)+PHEMA(**5**), only band-C was seen in its EEM and band-D appeared after 30-min-UV-irrad. In the upper solution, the ratio of band-B and band-C changed with UV-irrad., but only the weak edge was seen in the range of band-D. It should be the steric hindrance of the polymer. Benzene-rings could interfere with the hydrogen-bonding among Py-rings.

3.4. Complex formation between PVPys(**3**)+PVPhOH(**6**)

All samples showed precipitation and the precipitates were all colored in yellow or brown. EEMs of these solids showed weak UV-irrad.

effects (see Fig. 4). It could come from the extent of the ionization of N atom in Py-rings, as Zhou *et al.* reported[35]. In upper solution of P2VPy(3a)+PVPhOH(6), the significant emission bands of PVPhOH(6) (the same emission bands to the EEM of spin-coated PVPhOH(6), data not shown) is seen in lower part of the EEMs (in Figs. 4a) and 4b)), and no band-D was recognized both before and after UV-irrad. In lower solid phase of P2VPy(3a)+PVPhOH(6), emission bands of PVPhOH(6) could not be seen and strong band-B and band-C were seen (in Fig. 4c)). Though the dried solid (see Fig. 4d)) showed blue shifts of band-B and band-C, no change was seen with UV-irradiation (in Fig. 4e)).

Figure 4. EEMs of PVPy(3)+PVPhOH(6). a)~e): P2VPy(3a)+PVPhOH(6)(a): upper solution, b): upper solution with 30-min-UV-irrad., c): complex just after complex formation, d): dried, e): 30-min-UV-irrad.), f): P4VPy-St(3d)+PVPhOH(6), g),h): P4VPy(3a)+PVPhOH(6) solid (g): before and h): after 30-min-UV-irrad.)

Contrary to the samples which contain P2VPys (3a,3c), all samples that contain P4VPys(3b,3d) showed no obvious emission band in their EEMs. In the ranges of band-B and band-D₁, emission

bands appeared, and only in P4VPy(3b)(homopolymer)+PVPhOH(6) showed band-C. Benzene-rings of polystyrene part could interfere with the hydrogen-bonds among Py-rings, similar to the case of P2VPys(3a, 3c)+PHEMA(6).

4. Conclusions

Polymer complexes between PVPys(3) and two kinds of hydrogen-bond donating polymers were made and determined their luminescence.

The reason why the emission bands of PVPhOH(6) were seen only in the upper solution could be the high solubility of PVPhOH(6) in MeOH than PVPys(3) and PHEMA(5). In EEMs of PVPys(3)+PVPhOH(6), particularly in P4VPys (3b,3d) complexes, emission bands were seen in longer excitation wavelength region. It might correspond to the charge transfer complex formation in the solids before UV-irrad similar to DMP. The blue shift of the emission bands in P2VPy(3a)+PVPhOH(6)'s EEM would imply that the solvent residue and water in the solids play an important role in the ionization and relaxation in the excited states. In PHEMA(5) complexes, P2VPys(3a, 3c) showed larger UV-irrad. effect than P4VPys(3b,3d). In near future, we will elucidate the relationships between the extent of ionization and the luminescence of those polymer complexes.

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References

1. M.F.A. El-Sayed, M. Kasha, and Y. Tanaka, *J. Chem. Phys.*, **34**, 334 (1961).
2. I. Yamazaki and H. Baba, *J. Chem. Phys.*, **66**, 5826 (1977).
3. I. Yamazaki, K. Sushida, and H. Baba, *J. Chem. Phys.*, **71**, 381 (1979).
4. Y. Mochizuki, K. Kaya, and M. Ito, *J. Chem. Phys.*, **65**, 4163 (1978).
5. Y. Mochizuki, K. Kaya, and M. Ito, *J. Chem. Phys.*, **69**, 935 (1978).
6. S.F. Mason, *J. Chem. Soc.*, **1959**, 1240, 1247, and 1255.
7. J. S. Brinen, J. G. Koren, H. D. Olmstead, and R. C. Hirt, *J. Phys. Chem.*, **69**, 3791 (1965).
8. E.M. Kosower, *Topics Curr. Chem.*, **112**, 117 (1983).

9. M. Chachisvilis and A.H. Zewail, *J. Phys. Chem. A*, **103**, 7408 (1999).
10. M. Tsubouchi, *J. Phys. Chem. A*, **107**, 10897, (2003).
11. L. Ming-Fu, Y.A. Dyakov, C.-M. Tseng, A.M. Mebel, S.H. Lin, Y.T. Lee, and C.-K. Ni, *J. Chem. Phys.*, **123**, 054309 (2005).
12. S. Schlücker, M. Heid, R.K. Singh, B.P. Asthana, and J. Popp, W. Kiefer, *Z. Phys. Chem.*, **216**, 279 (2002).
13. I. F. Piérola, N. J. Turro, and P.-L. Kuo, *Macromol.*, **18**, 508 (1985).
14. P. Cáceres and I.F. Piérola, *Macromol. Chem. Rapid Commun.*, **8**, 573 (1987).
15. I.F. Piérola, M. Cáceres, P. Cáceres, M.A. Castellanos, and J. Nuñez, *Eur. Polym. J.*, **24**, 895 (1988).
16. M. R. Gómez-Antón, J. G. Rodríguez, and I. F. Piérola, *Macromol.*, **19**, 2932 (1986).
17. P. Cáceres, P. Pascual, A. Horta, and I. F. Piérola, *Polym. Prepr.*, **28**, 196 (1987).
18. T. Handa, Y. Utena, H. Yajima, and T. Ishii, *J. Phys. Chem.*, **90**, 2589 (1986).
19. T. Handa, Y. Utena, and H. Yajima, *J. Phys. Chem.*, **88**, 5150 (1984).
20. T. Handa, Y. Utena, H. Yajima, R. Katayama, T. Ishii, and T. Yamauchi, *J. Phys. Chem.*, **90**, 6324 (1986).
21. Y. Utena, H. Yajima, T. Ishii, and T. Handa, *Eur. Polym. J.*, **23**, 643 (1987).
22. Y. Utena, H. Yajima, T. Ishii, and T. Handa, *Eur. Polym. J.*, **24**, 71 (1987).
23. D. Vyprachtický, K.W. Sung, and Y. Okamoto, *J. Polym. Sci. Pt.A: Polym. Chem.*, **37**, 1341 (1999).
24. E. Vaganova, G. Meshulam, Z. Kotler, M. Rosenberg, and S. Yitzchaik, *J. Fluorescence*, **10**, 81 (2000).
25. E. Vaganova, S. Yitzchaik, *Polymeric Mater. Sci. Eng.*, **84**, 1089 (2001).
26. E. Vaganova, S. Yitzchaik, *224th ACS Nat. Meeting (Boston, USA), Abstr.*, POLY-058, (2004).
27. E. Vaganova, S. Yitzchaik, *Macromol. Symp.*, **207**, 95 (2004).
28. W.K. Fife, "Polymeric materials encyclopedia", J.C. Salamone *et al.* eds., CRC Press, Inc.: Boca Raton, pp. 7138 (1996), and references cited therein.
29. A.L. Weikel, S.D. Conklin, and J.N. Richardson, *Sens. Actuators B: Chem.*, **110**, 112 (2005).
30. S. Fujii, S.P. Armes, T. Araki, and H. Abe, *J. Am. Chem. Soc.*, **127**, 16808 (2005).
31. B.J. Kim, J. Bang, C.J. Hawker, E.J. Kramer, *Macromol.*, **39**, 4108 (2006).
32. J.N. O'Shea, Y. Luo, J. Schinadt, L. Patthey, H. Hillescheimer, J. Krempasky, D. Nordlund, M. Nagasono, P. A. Brühwiler, and N. Mårtensson, *Surf. Sci.* **486**, 157, (2001).
33. X. Zhou, S.H. Goh, S.Y. Lee, and K.L. Tan, *Appl. Surf. Sci.*, **119**, 60, (1997).
34. X. Zhou, S.H. Goh, S.Y. Lee, and K.L. Tan, *Polymer*, **39**, 3631, (1998).
35. X. Zhou, S.H. Goh, S.Y. Lee, and K.L. Tan, *Appl. Surf. Sci.*, **126**, 141, (1998).
36. M. Shibata, Y. Kimura, and D. Yagimura, *Polymer*, **45**, 7571, (2004).
37. K.Y. Wong, J. A.O. Smallfield, M. Fahlman, and A.J. Epstein, *Synth. Metals*, **137**, 1031, (2003).
38. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **16**, 173 (2003).
39. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **16**, 671 (2003).
40. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **17**, 87 (2004).
41. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **17**, 727 (2004).
42. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **18**, 109 (2005).
43. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **18**, 683 (2005).
44. S. Nishiyama, M. Tajima, and Y. Yoshida, *Thin Solid Films*, **509**, 177 (2006).
45. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **19**, 21 (2006).
46. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **19**, 727 (2006).
47. S. Nishiyama, M. Tajima, and Y. Yoshida, *J. Photopolym. Sci. Tech.*, **20**, 177 (2007).
48. S. Nishiyama, M. Tajima, and Y. Yoshida, *Colloid Surface A*, in press.
49. S. Nishiyama, M. Tajima, Y. Nakajima, T. Hanajiri, and Y. Yoshida, accepted to *Jpn. J. Appl. Phys.*
50. S. Nishiyama, M. Tajima, and Y. Yoshida, submitted to *Appl. Surface Sci.*
51. J.W. Hofstraat and U.P. Wild, "High-Resolution Excitation-Emission Matrices", chapter 16 in C. Gooijer, F. Ariese, and J.W. Hofstraat eds., "Shpol'skii Spectroscopy and Other Site-Selection Methods", *Chemical Analysis A Series of Monographs on Analytical Chemistry and Its Applications*, **156**, John Wiley & Sons, Inc., New York (2000).
52. B. Valeur, "Molecular Fluorescence", WILEY-VCH Verlag GmbH, Weinheim (2002).
53. S. Nishiyama, M. Tajima, and Y. Yoshida, unpublished results.