Luminescence Properties of Surface-modified Poly(4-vinylpyridine) Thin Films

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We have modified nitrogen-containing polymer surface by quaternization of nitrogen atoms with halogenated hydrocarbons. Previously, we used a few kinds of alkyl halides for surface quaternization. In this study, we varied the reagents for poly(4-vinylpyridine) (PVPy) quaternization and investigated the luminescence property of the surface quaternized PVPy. A variety of the quaternization reagents, halogenated hydrocarbons, revealed to be applicable for the quaternization to produce longer wavelength luminescence than the luminescence of non-quaternized PVPy films. The surface morphology of the films were also observed.

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

1. Introduction

Optical, luminescent and other properties of heterocycles, especially those of pyridine(1) have been attracted many photochemical and photophysical investigators[1-39]. Since the beginning of the last century, they knew the difference between the luminescence of pyridine(1) derivatives and that of their quaternized pyridinium derivatives(2), which reacted with alkyl halides or other halogenated hydrocarbons(3) [for 1: 25-27, for 2: 30-32]. A zwitterion or ion-pair is generated by nitrogen-quaternization with various halogenated hydrocarbons(3) as follows.

Scheme 1. Quaternization of pyridine(1)

In general, the positions of $n \rightarrow \pi^*$ [1-7] absorption band of pyridines(1) or quaternized pyridiniums(2), and the charge-transfer(CT) absorption band [8-23] of quaternized-

pyridiniums(2) are widely shifted according to solvent polarity. With these interesting features, various pyridinium derivatives(2) are widely used for the detection of solvent parameters, such as Z-value[13-17] and $E_T(30)$ -value[18,19]. The molecules which have high sensitivity to "solvent polarity" are called as "solvatochromic"[19]. This type of quaternization have also been done for polymeric materials, especially for poly(4-vinylpyridine)(PVPy)(4)[33-39]. The studies of its luminescence have been seldom[39], though PVPy(4) is commonly used among the numerous kinds of pyridine(1) derivatives. We had reported the change in the luminescent property[40] of PVPy(4) with the surface-quaternization of nitrogen atom using the vapor of ethyl bromide(3a), benzyl bromide(3b) or other halogenated hydrocarbons(3). The amount of quaternized pyridinium polymer(5a) was determined by means of UV-visible spectroscopy (for whole film) and XPS (for surface region of the film). The relationship between the emission intensity of pyridinium(2) at 500 nm (excitation at 300 nm) and the UV (absorbance at 300 nm) or XPS (~402 eV peak in N1s) signal intensity were almost linear in the surface quaternization to the

extent of 0 ~ 0.3[40]. The reaction scheme is as follows.

Scheme 2. Quaternization of PVPy (4)
(x : the extent of quaternization)

As PVPy(4) is also quaternized with alkyl halides(3) as shown in Scheme 2, the product polymer(5) would be expected to exhibit a solvatochromic property. Using this property, we can assume the polarity of the very neighbor of the chromophore in polymer. To use them for chemical sensors or some new devices, it is necessary to know the nature of luminescence of quaternized polymers(5). Our purpose is to develop an easy surface modification method using quaternization at gas/solid interface. In our previous study, the surface-quaternization process was achieved in a few hours or more exposure to the vapor of halogenated hydrocarbons(3). It is generally said that the generated ion pair is obstacle for the quaternization process in solution because of the charge repulsion of neighbor cations. For example, Kawaguchi *et al.* quaternized PVPy(4) by ethyl bromide(3b) to the extent of 10~35 % (mixture) at 46 °C for 5 days[38], and Arcus *et al.* described the conditions for quaternization of PVPy(4) with *n*-butyl bromide(3c) as to be kept at 60 °C for 4 days[34]. In our previous case, the ratio of the surface quaternization achieved to be 0.1 ~ 0.3 in 1 ~ 4 hours at 22 °C[40]. As this "only-surface" quaternization needs much less amount of reaction than the quaternization reaction in solution[40]. Though the amount is much less, the concentration at surface region is as high as liquid phase bulk-reaction.

In this study, we examined two kinds of dihalides, 1,3-dibromopropane(3d) and 1,2-dibromoethane(3e). Using these dihalides, cross-link reaction would be possible (see Scheme 3). This type reaction would be useful to reinforce films and to control its solubility to solvents, if they can be applicable to various polymers for the easy modification method.

Since the gaseous phase should contain smaller amount of charges than liquid phase, use

of gas/solid interface would be suitable for quaternization. To extend this gas/solid interface system, we examined various kinds of halogenated hydrocarbons(3) (see Formulae 1).

Scheme 3. Quaternization of PVPy (4) with
dihalogenated hydrocarbons (5)
(x, y : the extent of quaternization)

Formulae 1. Various halogenated hydrocarbons(3)

2. Experimental

2.1. Materials

PVPy(4) (Aldrich) was used after reprecipitation from methanol to diethyl ether. PVPy(4) was dried over 140 °C under deaerated condition. Ethyl bromide(3a) (98.0%, Kanto Chemicals Co., Inc.), *n*-butyl bromide(3c) (Nakarai Chemicals Ltd.), 1,3-dibromopropane(3d) (98.0%, Kanto Chemicals Co., Inc.), 1,2-dibromoethane(3e) (98.0%, Kanto Chemicals Co., Inc.), 2-bromopropane(3f) (Nakarai Chemicals Ltd.), cyclopropyl bromide(3g) (Tokyo Kasei Kogyo Co., Ltd.), 1-bromo-2-propene(3h) (98%, Tokyo Kasei Kogyo Co., Ltd.), and *n*-octyl bromide(3i) (Kanto Chemicals Co., Inc.) were used without further purification. Bromoacetic acid(3j) was mixed with water to use as a liquid reagent at room temperature. UV spectral grade methanol (Dojin) and HPLC grade diethyl ether (Wako) were used as supplied. The quartz plates (35×25×~1 mm³)

and glass cover slips ($18 \times 18 \times \sim 0.15 \text{ mm}^3$, for XPS) are used after cleaning.

2.2. Sample preparation

The sample films were prepared with the spin-coating method. The methanolic polymer solution ($\sim 0.5 \text{ g} / \sim 5 \text{ mL}$) was dropped on the cleaned glass plates on the spin-coater and coated PVPy(4) at 1500 rpm for 60 s, and then dried over 140°C about 1 h under deaerated condition. PVPy(4) films showed an absorption band which has a few peaks[39,40] around 260 nm. All films were roughly sub- μm thick (not determined).

2.3. Quaternization process

Inside the closed glass dishes, spin-coated PVPy(4) films and a small bowl of liquid halogenated hydrocarbons(3) were placed as shown in Fig.1. The space in glass dishes was filled with halogenated hydrocarbon(3) vapor during quaternization.

Fig. 1. Setup for quaternization procedure.

2.4. Measurements of properties of various quaternized PVPy(5)

UV-visible absorption spectra were measured with a double beam UV-visible spectrophotometer, U-2001 or UV-3200 (Hitachi). For luminescence spectra, an F-4010 fluorescence spectrophotometer (Hitachi) with options for solid samples was used. All atomic force microscopy (AFM) images were acquired at a scan rate of $\sim 1 \text{ Hz}$, using SPI3700 and SPA-300 (Seiko Instruments) with dynamic force mode (DFM) option. Silicon tips ($f = 133 \text{ kHz}$, $C = 12 \text{ N} / \text{m}^2$) for DFM were employed for non-contact mode detection. X-ray photoelectron spectra were recorded with an ESCA 750 electron spectrometer (Shimadzu), using C_{1s} peak (285 eV) as a standard for charge correction.

3. Results and Discussion

3.1. UV-visible and luminescence measurement of PVPy(4) and quaternized PVPy(5) films reacted with various halogenated hydrocarbons(3)

Quaternization was achieved with 8 kinds of halogenated hydrocarbons(3e~3j). They are normal alkyls, branched alkyl, cycloalkyl, olefinic hydrocarbons and carboxylic acid. The quaternization ratio was not seemed to decrease with increase of molecular weight and decrease of vapor pressure at room temperature, the depth of permeation. Obtained UV-visible and luminescence spectra (excited at 300 nm) were shown in Fig.2.

Fig. 2. UV-visible and luminescence spectra of a) PVPy(4)(UV-vis: —; luminescence: ---) and PVPy(5) (UV-vis: —; luminescence:) quaternized with a) *n*-butyl bromide(3c), b) *n*-octyl bromide(3i), c) 2-bromopropane(3f), d) cyclopropyl bromide(3g), e) 1-bromo-2-propene(3h), f) 1,2-dibromoethane(3e), g) 1,3- dibromopropane(3d), and h) Bromoacetic acid(3j).

New emission bands appeared in the visible region for all quaternized PVPy(5) in Figs. 2a~h). Brinen *et al.* reported that the CH₃Br salt of pyridine showed luminescence at $\sim 19400\text{ cm}^{-1}$ ($\sim 513\text{ nm}$)[30]. The new emission band in our case is similar to them. The broad and relatively

weak band near UV region is the original emission of PVPy(4)[40]. New luminescence band was seemed to be varied with not the molecular weight, but the structure of halogenated hydrocarbons(3). In Figs. 2b), c) and g), the original emission band around 390 nm remains. It would be due to the depth that reaction occurred in PVPy(4) films.

The most remarkable difference among reacted PVPy(5) films was the wavelength of new emission band in case of cyclopropyl bromide(3g) (seen in Fig. 2d)). It was located at 550 nm (50 nm longer than ethyl bromide(3a) and many other halogenated hydrocarbons(3)). To compare with ethyl bromide(3a), a few of other halogenated hydrocarbons(3c~f,h~j) showed new emission bands at relatively shorter than 500 nm. Though emission intensity is difficult to compare with each other because of the scattering or reflex on films, the intensity of this new band also seemed to change according to the difference of the nature of halogenated hydrocarbons(3). The intensity of new emission did not depend on the yield of quaternization reaction. In cases of *n*-octyl bromide(3i), cyclopropyl bromide(3g), 1-bromo-2-propene(3h), 1,3-dibromopropane(3d), 1,2-dibromoethane(3e) and 2-bromopropane(3f), the change of emission could be due to some reaction occurred between the quaternization procedure (for example, ref.[41]). Especially in case of bromoacetic acid(3j)[42], the shorter wavelength could be due to water concluded in bromoacetic acid(3j) mixed with water. PVPy(5j) shows strong CT band, though the counter anion exchange is possible between acid anion with Br⁻.

3.2. AFM measurement of PVPy(4) and quaternized PVPy(5) films

The morphology was determined for each of reacted PVPy(5) film. The AFM images were shown in Fig. 3 (as typical reacted PVPy(5), cases of cyclopropyl bromide(3g) and 1,3-dibromopropane(3d) were shown).

Fig. 3. AFM images of a) PVPy(4) and PVPy(5) reacted with b) cyclopropyl bromide(3g) and c) 1,3-dibromopropane(3d). The square is $200 \times 200 \text{ nm}^2$.

The quaternization results of PVPy(5) films reacted with halogenated hydrocarbons(3c~j) are shown in Table 1. XPS results were discussed in the next paragraph. All of the listed halogenated hydrocarbons(3) changed PVPy(4) luminescence property and the morphological change was observed in $200 \times 200 \text{ nm}$ region. Small lumps of $10 \sim$ several hundred nm were seen on the surface of reacted PVPy(5) films. The flat surface was changed to be rough with quaternization. The morphological change in large scale such as $1 \times 1 \mu\text{m}^2$ was not so significant. It would be due to the hydrophobicity of carbon chain structures in halogenated hydrocarbons(3c~j). From Q_s values (discussion about Q_s is in the next paragraph), ϵ of each quaternized PVPy(5) was found to be much different. For example, the ratio of Q_s , for quaternized PVPy(5) films for *n*-octyl bromide(3i) in this study and benzyl bromide(3b) in the previous study[40], Q_s , was calculated to be ~ 0.9 . Those kinds of halogenated hydrocarbons(3) would be useful for the surface protecting materials for nitrogen-containing polymers.

Table 1. The changes of PVPy(4) with quaternization using various kinds of halogenated hydrocarbons.

Halogenated hydrocarbons	Vapor pressure k Pa / (mmHg) ¹ boiling point* °C ²	Absorption change at 300 nm (ΔAbs_{300}) with quaternization ³	Q_s^4 (Br/N) ⁵ reaction time	The luminescence change observed at 300 nm excitation ⁶
ethyl bromide ⁶	55.6 (417.3) (38.4*)	0.446	0.30 (0.37) 4 hours	390 nm ▼▼ 500 nm ▲
<i>n</i> -butyl bromide	4.73 (35.5) (91.7*)	0.037	0.31 (0.29) 2.5 days	390 nm ▼▼ 500 nm ▲
<i>n</i> -octyl bromide	- (199*)	0.015	0.84 (0.83) 1 month	390 nm ▼ 480 nm ▲
2-bromopropane	16.15 (121.1) (70.3*)	0.01	0.52 (0.44) 1 week	390 nm ▼ 500 nm ▲
cyclopropyl bromide	- (69*)	0.224	0.46 (0.37) 1 day	390 nm ▼▼ 550 nm ▲▲
1-bromo-2-propene	- (70.28*)	0.19	0.93 (0.86) 1 day	390 nm ▼ 485 nm ▲
Bromoacetic acid	0.0117 (0.088) (203*)	> 3	0.85 (0.54) 3.5 days	390 nm ▼ 495 nm ▲
1,2-dibromoethane	1.59 (11.9) (131*)	0.95	0.25 (0.17) 12 hours	390 nm ▼▼ 500 nm ▲
1,3-dibromopropane	0.31 (2.3) (167*)	0.80	0.47 (0.42) 1 day	390 nm ▼▼ 494 nm ▲

¹ mmHg, 22°C, under atmospheric pressure (*b.p.); ² ref.43, ³ Each value is only an example and it was obtained for each reaction time (not same) at room temperature; ⁴ the ratio of surface quaternization; ⁵ the ratio calculated from the value of XPS quantitative calculation; ⁶ ▼: the emission band disappeared; ▲: new emission band appeared; ⁷ ref.40

Though the reaction mechanism is not clear, the morphologies of the film surfaces were approximately same and the change of the morphology would be correspond to the chemical change on the film surfaces.

3.3. XPS measurement of quaternized PVPy(5)

Each obtained spectrum was not shown, as typical XPS spectra, N_{1s} and Br_{3p} spectra of two halogenated hydrocarbons were shown in Fig.4, and all the resulted values of surface quaternization and the ratio of surface Br and N were shown in Table 1.

Fig. 4. Typical a) N_{1s} and b) Br_{3p} spectra of quaternized PVPy(5) of i) 1,3-dibromopropane(3d) and ii) *n*-octyl bromide(3i).

N_{1s} spectrum of PVPy(4) has only one peak at ~399 eV[40], and no peak appears in Br_{3p} spectrum of PVPy(4)[40]. From N_{1s} peaks as seen in Fig. 4a), the surface quaternization ratio: Q_s was calculated (the ratio of the peak at ~402 eV and the peak at ~399 eV) and those values were listed in Table 1. From these values, we can

assume that the surface quaternization would occur completely at room temperature. In addition to Q_s , the surface atomic ratio was also listed in Table 1. If these two values (Q_s and Br/N) is much different, it would be the loss of Br^- , displaced by other anions. If the neutral Br peak is shown in Br_{3s} , Br_{3p} or Br_{3d} spectra, it corresponds to the adsorption of the halogenated hydrocarbon(3) molecules on the film surface. In this study, no significant case was found. Only slight amount of neutral molecules were found. For example, both i) and ii) Br_{3p} spectra in Fig. 4b) contain very small peaks of neutral molecules at higher energy region of anion peaks. The estimation of this small amount of neutral Br atom is not possible, because of the lowliness of spectral resolution. We would make another attempts in future. The small amounts of Br mean that the reactivity of these halogenated compounds(3) is high. In case of bromoacetic acid(3j), the difference between Q_s and Br/N was much larger than other halogenated hydrocarbons(3). The reacted bromoacetic acid(3j) molecule binding to the pyridinium(5j) ring in the quaternized PVPy(5j) films might have ionized and have replaced Br^- as counter anion.

4. Conclusions

Various kinds of spectra (UV-visible, luminescence, and XPS) of PVPy (4,5) films were measured before and after the surface quaternization of PVPy (5) films. From these results, we confirmed the progress of the surface quaternization. In this study, many kinds of halogenated hydrocarbons were found to be useful and hopeful for the surface quaternization. For example, both Br atoms in dihalides of halogenated hydrocarbons(3d,e) was easily react with pyridine moieties of PVPy(4) to introduce bridging structure. It would expand this method widely to produce new functional materials, such as chemical sensors, photo or optical filters, and other functional membranes, in future.

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