Photometric Characteristics of Aqueous Solutions and Polymer Films Containing Bromothymol Blue/Diphenyliodonium Salts Applied for UV Monitoring

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(Received 26 November 2014; Accepted 9 January 2015; Published 31 January 2015)

We examined the photometric characteristics of ultraviolet light (UV) measurements of aqueous solution and polyvinyl alcohol (PVA) film containing bromothymol blue (BTB) and diphenyliodonium salts (chloride, nitrate and trifluoromethane sulfonate). The solution and film were initially green (neutral), but were changed to yellow (acidic) by irradiation with 254 nm UV from a mercury lamp. A solution and film containing only BTB did not show the color change, which we concluded was solely induced by the acid generation from the diphenyliodonium salts. Photochemical kinetics of the UV-induced color change are discussed on the basis of experimental results; the color change proceeded obviously according to pseudo-first-order kinetics. This BTB/diphenyliodonium salt system could be used as a low-cost, mobile UV dosimeter. [DOI: 10.1380/ejssnt.2015.15]

Keywords: Photochemistry; Photon absorption spectroscopy; Visible/ultraviolet absorption spectroscopy; Bromothymol blue; Diphenyliodonium salt

I. INTRODUCTION

The monitoring of ultraviolet light (UV) is important from the viewpoint of human health. Excessive exposure to UV from the sun can result in various undesirable effects on human skin and eyes [1]. For example, it is well known that UV radiation causes sunburn, and that excess doses of UV may result in pain, blisters, and peeling skin. Skin cancer is a more severe disease induced by UV irradiation. Basal cell carcinoma, squamous cell carcinoma, and malignant melanoma are common forms of serious skin cancer. In particular, non-melanoma cancers are strongly believed to be the result of UV exposure. Damage to eye tissue (lens, cornea and retina) is also caused by exposure to UV. It is therefore important to carefully monitor the UV dose on human skin. For routine monitoring of incident UV dose, a dosimeter should be light, small, and mobile. Of course, the measured dose should also be sufficiently accurate.

One of the candidates for a mobile UV dosimeter is dyed polymer film. Many studies on the fabrication and dosimetric characteristics of dyed polymer films have been reported. For example, Abdel-Fattah et al. described the fabrication and evaluation of various dyed polymer films for UV monitoring [2–7]. They mainly used polyvinyl alcohol (PVA) as a matrix of UV-responsible dyes. Mills et al. reported that colorless PVA films containing neotetrazolium chloride turned red by UV illumination [8]. Kozicki and Sasiadek employed polyamide fabric as a matrix polymer and used nitro blue tetrazolium chloride as an active component [9].

In this study, we used mixtures composed of photochemical acid generators (diphenyliodonium salts) and an acid-base indicator (bromothymol blue) to monitor UV dose. Photochemical acid generators are key chemicals in the electronic device industry, which employs processes of chemically amplified positive and negative photoresists for photolithography. Chemically amplified resists are decomposed or cross-linked by the reaction of photochemically generated acid, and the pattern of the desired electronic circuit is then formed by subsequent chemical treatment. This type of photoresist is highly sensitive, and so can be applied to UV dosimetry as well.

II. EXPERIMENTAL PROCEDURE

A. Reagents

The chemicals used were bromothymol blue (BTB), polyvinyl alcohol (PVA), diphenyliodonium chloride (DIC), diphenyliodonium nitrate (DIN), diphenyliodonium trifluoromethane sulfonate (DIT), and ethanol. All were purchased from Wako Pure Chemicals, Co. Ltd., Japan, and used without further purification. Figure 1 shows the chemical structures of BTB, DIC, DIN and DIT.

FIG. 1. Chemical structures of BTB, DIC, DIN and DIT.
B. Preparation of stock solution

First, BTB (0.02 g, $3.2 \times 10^{-5}$ mol) was dissolved into a water (60 mL)/ethanol (5 mL) mixed solution at room temperature. One of the diphenyliodonium salts (abbreviated as DIS, $3.0 \times 10^{-5}$ mol) was also dissolved into a water (10 mL)/ethanol (5 mL) mixed solution, and the BTB solution (3 mL) was added into the prepared diphenyliodonium solution. The BTB/DIS solution was shielded from light with aluminum foil.

C. Preparation of PVA film containing BTB and DIS

PVA (1 g) was dissolved in water (40 mL) by stirring at 90°C for 3 h; the solution was then successively stirred at room temperature until PVA was completely dissolved. The BTB/DIS solution was then poured into the PVA solution. This BTB/DIS/PVA solution (1 mL) was placed on a glass piece $(2 \times 2 \text{ cm}^2)$ and a thin film was fabricated by spin coating (AIDEN SC2005). A thin film consisting of BTB and PVA (without DIS) was also made in the same manner.

D. UV irradiation and measurement of visible absorption spectra

Irradiation of the solutions and PVA films with UV light was carried out with a low-pressure mercury lamp (Hamamatsu Photonics L937-02). Wavelength of the UV light was 253.7 nm. The BTB/DIS solutions were irradiated in a quartz cuvette (light path length: 1 cm) for 1-30 min at room temperature. Intensity of the incident UV light was measured using a portable illumination photometer. After irradiation, visible absorption spectra were measured with a double beam visible spectrophotometer (Shimadzu UV-160 A) in the wavelength range of 400-800 nm.

The PVA films were irradiated in the same manner for 1-50 min, and absorption spectra were measured. The reference used to measure the absorption spectra of the samples was PVA film fabricated without BTB/DIS. The reference and sample films were fixed on a sample folder of the spectrometer using scotch tape pieces. Spectra were measured in the wavelength range described above (400-800 nm).

III. RESULTS AND DISCUSSION

A. Photo-induced color change of BTB/DIS solutions

Figure 2 shows the typical visible absorption spectra of the BTB/DIC solution irradiated for 0-30 min. The UV irradiation caused an obvious change in the spectra. Two absorption maxima were observed at 623 nm and 430 nm. These maxima are the absorption peaks of BTB. The absorbance of the peak at 623 nm lessened, while that at 430 nm increased with UV irradiation. These changes corresponded to the color change of the solution from green to yellow. The result indicated that UV irradiation caused acid generation, resulting in the color change of BTB.

An isosbestic point of the spectra was observed at 500 nm. This indicated that the concentration of BTB during UV irradiation was constant. Here, the concentrations of green and yellow forms of BTB are represented by $C_G$ and $C_Y$, respectively, and their molar extinction coefficients are represented by $\varepsilon_G$ and $\varepsilon_Y$. Based on the Lambert-Beer’s law, absorbances of green and yellow forms $A_G$ and $A_Y$ are given as follows:

$$A_G = C_G \cdot \varepsilon_G \cdot L \quad \text{(1)}$$

$$A_Y = C_Y \cdot \varepsilon_Y \cdot L \quad \text{(2)}$$

where $L$ is the light path length. The observed absorbance $A$ is the sum of $A_G$ and $A_Y$. If the total concentration $C$ ($C = C_G + C_Y$) is constant during UV irradiation, $A$ is given by the following relationship:

$$A = A_G + A_Y = C_G \cdot \varepsilon_G \cdot L + (C - C_G) \cdot \varepsilon_Y \cdot L$$

$$= C \cdot \varepsilon_Y \cdot L + C_G \cdot (\varepsilon_G - \varepsilon_Y) \cdot L \quad \text{(3)}$$

If $\varepsilon_G$ and $\varepsilon_Y$ are equal at a wavelength, the second term of equation (3) is zero, and $A$ does not depend on $C_G$ and $C_Y$. Therefore, an isosbestic point appears at this wavelength. Thus, BTB is not decomposed or changed to other products with UV light, but is the sole cause of the conversion between its green form and yellow form.

Absorption spectra of the solutions containing DIS other than DIC were also measured. The observed transformation rates of the spectra were almost the same as those of the spectra of the BTB/DIC solution. This indicated that the rate of photochemical acid generation from the three DIS used in this work were almost equal. To check if the acid generation from the solvent and/or BTB molecule itself were negligible or not, absorption spectra of the BTB solution without DIS were also measured. The spectra are shown in Fig. 3; as is clear in the figure the spectra did not change by UV irradiation. Acid generation from molecules other than DIS was therefore considered negligible and ignored. The color change of BTB...
was induced solely by photochemical acid generation from DIS.

Absorbances at 623 nm of the spectra of the BTB/DIS solutions are plotted as a function of incident UV dose. Figure 4 shows the logarithmic plot of absorbance at 623 nm as a function of incident UV dose observed using the BTB/DIC solution. The relative absorbance $A/A_0$ means the ratio of the absorbance measured at each incident dose to that measured before UV irradiation. Decay of $A/A_0$ is well fitted to an exponential function, indicating that efficiency of the photo-induced color change of BTB can be represented by first-order kinetics. Here, if the photochemical acid generation from DIS is assumed to be a first-order reaction, the rate of acid generation is represented by the following rate equation:

$$\frac{dC_{\text{DIS}}}{dt} = I \cdot \Phi \cdot \varepsilon \cdot C_{\text{DIS}}$$  \hspace{1cm} (4)

where $C_{\text{DIS}}$ is the concentration of DIS, $t$ is time, $I$ is the intensity of incident UV light, $\Phi$ is the quantum efficiency of the acid generation, and $\varepsilon$ is the molar extinction coefficient. Representing $C_{\text{DIS}}$ at time zero as $C_{\text{DIS,0}}$ and integrating the above rate equation, we obtain:

$$\frac{C_{\text{DIS}}}{C_{\text{DIS,0}}} = e^{-I \cdot \Phi \cdot \varepsilon \cdot t}$$  \hspace{1cm} (5)

The incident UV dose $D$ can be represented by the product of $I$ and $t$. The above equation is thus converted to the following equation:

$$\frac{C_{\text{DIS}}}{C_{\text{DIS,0}}} = e^{-\Phi \cdot \varepsilon \cdot D}$$  \hspace{1cm} (6)

We here assume that acid generated from DIS immediately reacts with BTB molecules and inducing the color change of BTB; the change of $C_{\text{DIS}}$ exactly corresponds to the change of $C_{\text{G}}$. Since $C_{\text{DIS}}$ is much higher than $C_{\text{G}}$ in the present case, the reaction between BTB and acid generated from DIS can be treated as a pseudo-first-order reaction. The observed decay curve of $C_{\text{G}}$ is reasonably explained under this assumption:

$$\frac{C_{\text{G}}}{C_{\text{G,0}}} = e^{-k \cdot D}$$  \hspace{1cm} (7)

where $C_{\text{G,0}}$ is the initial $C_{\text{G}}$, and $k$ is the pseudo-first-order rate constant of the color change of BTB. $C_{\text{G}}$ and $C_{\text{G,0}}$ are related to the absorbances $A$ and $A_0$ (the initial absorbance) at 623 nm, respectively. Hence the following equation is obtained:

$$\frac{A}{A_0} = e^{-k \cdot D}$$  \hspace{1cm} (8)

The line shown in Fig. 4 drawn on the basis of equation (8) reproduces the decay of $A/A_0$ quite well. This indicates that the BTB/DIS systems respond quantitatively to the UV dose.

B. Photo-induced color change of BTB/DIC/PVA films

Figure 5 shows the typical visible absorption spectra of the BTB/DIC/PVA film irradiated for 0–50 min. The spectra of the film essentially reproduce the features of the spectra obtained for BTB/DIC solution; two absorption peaks were observed at the wavelengths around 430 and 620 nm. The absorbance of the peak at 620 nm lessened, while that at 430 nm increased with UV irradiation. This result indicated that chemical processes similar to those observed for the BTB/DIC solution also occurred in the PVA film containing BTB and DIC. The absorption spectra of the BTB/PVA film (without DIC) irradiated were measured in the same manner to check if the acid generation from PVA was negligible or not. The spectra in this film scarcely changed by UV irradiation. The acid generation from PVA was hence ignored, and the color change of the film was considered to be due solely to the acid generation from DIC. Based on the results described above, the photometric characteristics of the films were found to be quite similar to those of the BTB/DIC aqueous solutions. Comparing the absorbance change observed for the film with that observed for the solution, it was apparent that the irradiation time course of the film absorbance...
was not perfectly linear. This deviation of the absorbance may have been caused by unevenness in the film thickness; each absorbance was measured using a separate film. At this time, it is difficult to make the films perfectly uniform in thickness with the process used, and their thickness often fluctuated. The BTB-dyed film examined in this work will be a good UV dosimeter if the film fabrication processes can be improved. Seeking such improvement will be a task of future research.

IV. CONCLUSIONS

In this work, the photometric characteristics of BTB/DIC aqueous solutions and BTB/DIC/PVA films were studied. These systems (solutions and films) showed similar spectral characteristics. In the case of the solution, absorption maxima were observed at 623 and 430 nm. The absorbance at 623 nm decreased with successive irradiation of 254 nm UV, while the absorbance at 423 nm increased. The color changed from green to yellow with UV irradiation. An isosbestic point was observed at 500 nm in the absorption spectra; the total concentration of green and yellow forms of BTB remained constant during the color change. The observed UV-irradiation time course of the absorbances was explained on the basis of first-order kinetics. Therefore, the relationship between color and irradiated UV dose was clearly represented, and the system is thought to be a possible candidate for a low-cost, mobile UV dosimeter.

In this study, only UV-C (wavelength: 254 nm) was employed as a test light to irradiate the film. However, in the sunlight reaching the earth’s surface, UV-A (wavelength: 315-400 nm) and UV-B (wavelength: 280-315 nm) are especially abundant. Therefore, UV-A and UV-B both seriously influence human health and degradation characteristics of industrial materials. The dosimetric characteristics related to UV-A and UV-B should therefore be examined. Another important issue that remains to be solved is a process for making films of uniform thickness. This should be clarified by the improvement of the fabrication process. Other subjects to be elucidated include stability of the coloration, temperature dependence of the photometric characteristics, and the relationship between the photometric characteristics and the combination of dyes (in this work BTB) + acid generators (in this work DIC).

ACKNOWLEDGMENTS

This work was financially supported by the Foundation for Applied Research and Technological Uniqueness at Nagaoka University of Technology, Japan and the Institute of National College of Technology, Japan.