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Photo- and Radiochromic Properties of Diarylethene Films with Surface Functionality

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Diarylethene, 2-bis [2-methyl-5-(5-trimethylsilylthiophen-2-yl) thiophen-3-yl]-3, 3, 4, 4, 5, 5-hexafluorocyclopentene, films were fabricated by the conventional vacuum deposition method, and evaluated for their photochromic and radiochromic properties. The absorbance at 620 nm was increased by 365 nm UV exposure and decreased by visible light exposure at 550 nm. In the colorless state, crystallization was observed on the film surface kept at 50 ℃ for 1 day. In contrast, no such crystallization was observed in the colored state. The absorbance at 310 nm decreased upon X-ray exposure to the colorless film. The colorless state showed a linearity between the absorbance and X-ray dose, and the measurable dynamic range was 0.1–1000 mGy.

1. Introduction

Dosimetric materials have been widely utilized in various fields of radiotherapy[1–3] and personal monitoring,[4–6] which require tissue equivalence of the materials. In particular, the effective atomic number (Z_{eff}) involved in the interaction probability with ionizing radiation should be as low as those of human tissues. There are many types of materials utilized in the fields when categorized by the phenomena used for measurements, for example, thermoluminescence,[7–11] optically stimulated luminescence,[12–16] and radio-photoluminescence types.[17–24] Among them, Mn-doped $Li_2B_4O_7$[25] and BeO,[26] which have low Z_{eff} (~7–9), have been commercially used owing to their tissue equivalency.

In addition to these phosphors, film-badge-type dosimeters using radiochromism have been expected owing to their high tissue equivalence.[27–31] Particularly in organic compounds, chromism is defined as a reversible isomerization between two isomers induced by external stimuli such as light. In this phenomenon, energy deposition on the material is important, and energy deposition also occurs upon the irradiation of ionizing radiations. Therefore, some photochromic materials have been utilized in radiation measurements since certain materials can undergo radiochromism, which is a kind of photochromism induced by ionizing irradiation.[32–34] The desired characteristics for chromic materials are as follows: high thermal

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stability in both isomers, high fatigue resistance for repeatability, and high sensitivity and reactivity.

Diarylethenes are representative P-type chromic molecules that satisfy the above characteristics and have low Z_{eff} owing to their composition of light elements such as H, C, N, and O.[35] Various diarylethene compounds have been developed by some research groups and applied to radiochromic dosimeters.[36–38] For example, Asai *et al.* have reported that polymer films consisting of P-type diarylethene molecules, 2, 3-bis (2, 4, 5-trimethyl-3-thienyl) maleimide, showed good radiochromic properties under X-ray irradiation from low to high dose distributions.[39] In the study, photochromic diarylethene, 1, 2-bis [2-methyl-5-(5-trimethylsilylthiophen-2-yl) thiophen-3-yl]-3, 3, 4, 4, 5, 5-hexafluorocyclopentene (DAE), films with high thermal stability of both isomers, fatigue resistance for repeatability, and high sensitivity and reactivity were synthesized.[40–42] Photochromic and radiochromic properties of DAE films under UV–visible and X-ray irradiation were investigated.

2. Materials and Methods

Amorphous DAE films were prepared following the method used in a past study.[43] The thickness of the film mounted on a glass substrate was controlled to be 40–50 nm. The measurement of diffuse transmission spectra was performed using a spectrophotometer (SolidSpec-3700, Shimadzu) to determine the absorbance. The photochromic reaction was induced by UV exposure (365 nm) using a UV lamp (300 μW/cm^2, LUV-16, AS ONE) and visible light exposure (550 nm) using a light source (30 mW/cm^2, KTS-150RSV, Tokina) with a filter (HMX0550, Asahi Spectra). An X-ray generator composed of an X-ray tube (XRB80P&N200X4550, Spellman), a tungsten target, and a beryllium window was used as the exposure source. The applied voltage to the X-ray tube was set to 40 kV. The dose rate was 50.7 Gy/h when the tube current and voltage were 5.2 mA and 40 kV, respectively.

3. Results and Discussion

Figures 1(a) and 1(b) respectively show the changes in absorption spectra of the colorless and colored DAE films with the exposure time. The absorbance at 620 nm increased with the UV exposure time. The absorption at 400 nm derived from the $\pi \rightarrow \pi^*$ transition of thiophene parts was observed only in the colored state. The absorption wavelength was consistent with the reported one.[44] The photostationary (PSS) state was obtained after the 300 s UV light exposure of the colorless film, with no significant change in absorbance after this duration. On the other hand, the absorbance at 620 nm decreased when irradiated with visible light at 550 nm. The initial colorless state was obtained after 690 s of visible light irradiation to the PSS state. The isomerization time from colored to colorless states was longer than that from colorless to colored ones. These colorization and decolorization reactions could be repeated several times, and no change in intensity was observed. This result indicated that the DAE films had fatigue resistance for repeatability.

Figures 2(a) and 2(b) respectively show photographs of DAE films before and after annealing at 50 °C for the films under crossed-nicols observation. In the photographs, the dark and bright

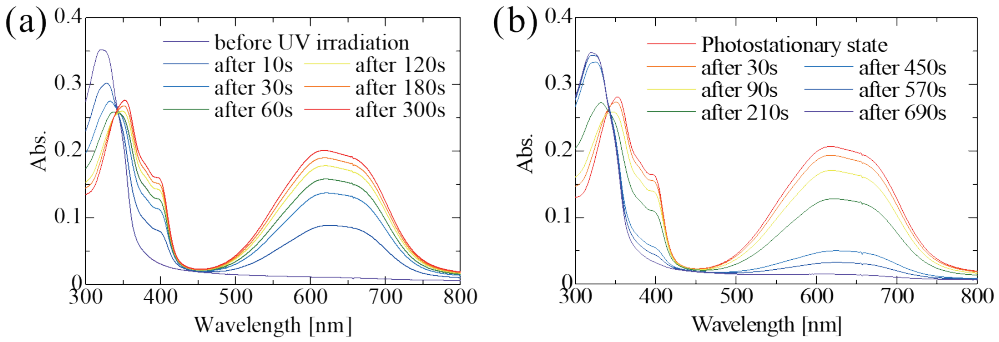

Fig. 1. (Color online) Changes in absorption spectra of colorless (a) and colored (b) DAE films under UV (365 nm) and visible light (550 nm) irradiation.

areas correspond to the amorphous and crystallized areas, respectively. The colored state showed no crystallized areas after annealing for 24 h, while the colorless state showed crystallized areas distributed over the entire film surface. This difference would be due to the difference in the glass transition temperature (T_g). According to past studies, the T_g of the colorless state (32 °C) is lower than that of the colored one (94–95 °C),[45–47] making the molecular motion in the colorless state more active than that in the colored state at the same temperature. Therefore, the transition from a metastable amorphous state to a stable crystalline state was observed only in the colorless state, as indicated by the active molecular motion due to the lower T_g. These results suggest that the colorless film exhibits better radiochromic properties in response to energy transfer from radiation.

Figure 3(a) shows the changes in the absorption spectra of the colorless film irradiated with X-rays at different doses. The inset shows the enlarged view of the spectra at 310–330 nm. The absorbance at 320 nm decreased with increasing X-ray dose. The change in absorbance was different from those under UV and visible irradiations shown in Fig. 1. This result indicates that the X-ray exposure of the colorless films induced changes in molecular structure or other characteristics, which were different from those observed under UV and visible light irradiation. The origin of the changes in the absorption spectra would be the same as that previously reported.[44] Figure 3(b) shows the dose dependence of absorbance (Δ absorbance), which is defined as an increase in absorbance from that before X-ray irradiation. The sample after 1000 mGy exposure reached the PSS state when irradiated with UV light. The PSS state returned to the initial state upon irradiation with visible light at 550 nm. The colorless state showed sublinearity between the dose and the absorbance in accordance with the fitting formula ($y = ax^b$, where a and b were constants), and the dynamic range was 0.1–1000 mGy. Additionally, the calculated R^2 value of the colorless state was 0.9979. The lower detection limit was inferior to that of the C-doped Al_2O_3 crystal, which is a commercial dosimetric material (0.01 mGy).[48] One example of an approach to improving radiosensitivity is the addition of phosphors as energy carriers to DAE films. In a past study, the addition of phosphors into diarylethene films improved the radiochromic properties owing to the energy transfer from the phosphors to the diarylethenes.[39]

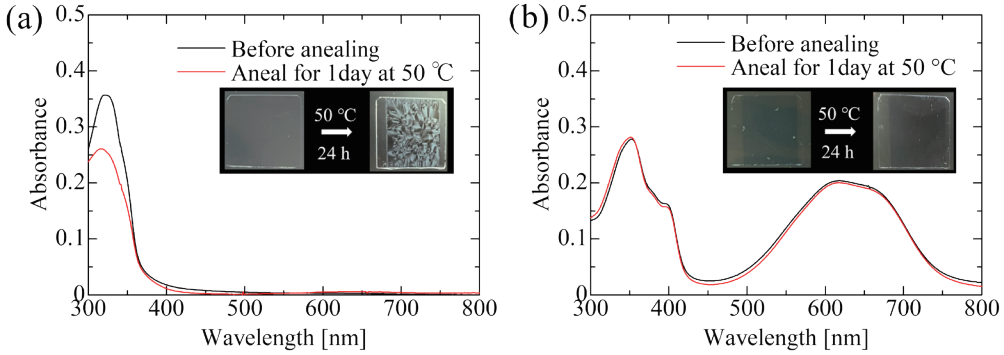

Fig. 2. (Color online) Changes in absorption spectra of (a) colorless and (b) colored DAE films when kept at 50 ℃ for 1 day. The insets show the corresponding photographs of the DAE films.

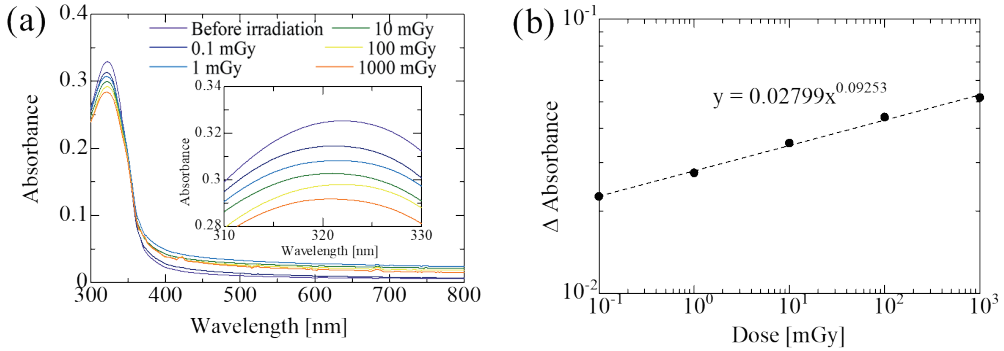

Fig. 3. (Color online) (a) Changes in absorption spectra of a colorless DAE film irradiated with X-rays at different doses and (b) dose dependence of absorbance at 320 nm.

4. Conclusions

DAE films were fabricated by the conventional vacuum deposition method. The colorless and colored DAE films exhibited high photosensitivity to UV and visible light irradiation, and high fatigue resistance for repeatability. The surface functionality of the films was observed only in the colorless state after being kept at 50 ℃ for 1 day, likely owing to the active molecular motion associated with the lower T_g. The colorless films showed good linear relationship between the absorbance change and the X-ray dose, and the dynamic range was 0.1–1000 mGy.

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