

The Radiation-Induced Coloration of Amorphous Photochromic Dithienylethene Films

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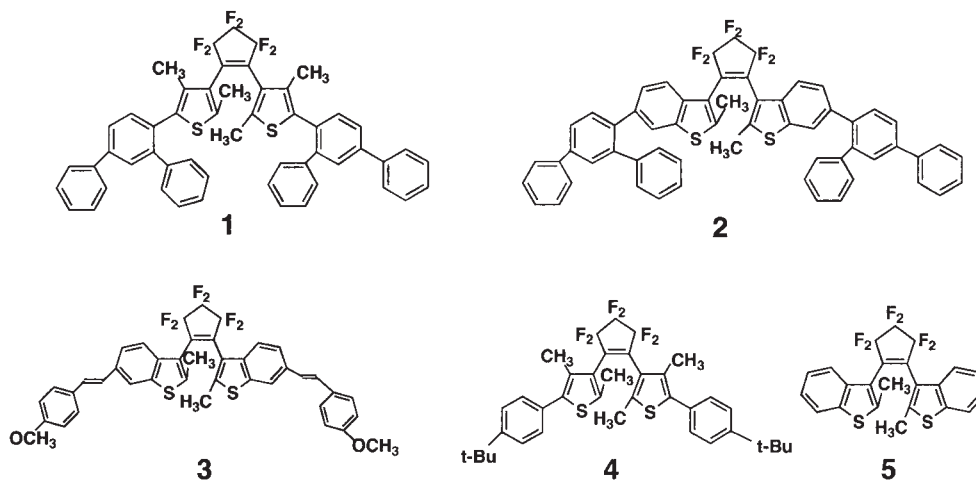
The radiation-induced coloration of bulk amorphous films of five photochromic diarylethenes was studied with the aim of developing reusable, sensitive color dosimeters. The films contain an extremely high concentration of diarylethenes. The most intense coloration was observed for the film containing 1,2-bis(2,4-dimethyl-3-thienyl)perfluorocyclopentene having 3-phenyl-4-diphenyl substituents. The color disappeared upon irradiation with visible light. The coloration increased linearly with an increase in the absorbed dose up to 3000 Gy. The relative sensitivity of radiation-induced coloration among the five derivatives qualitatively agreed with the sensitivity of photo-induced coloration from UV light (254 nm) irradiation.

Dosimeters based on radiation-induced coloration are used extensively to monitor radiation doses in the radiation processing industry in such processes as radiation curing and the radiation sterilization of medical products.¹ The chemical dosimeters developed so far are based on color changes induced by reactions triggered by radiation-generated acids or radicals.^{2–4} Another type of color dosimeter is based on diacetylenes. The color change in this case is due to radiation-induced solid state polymerization of the diacetylenes.⁵ Although these color dosimeters are widely used, they suffer from low sensitivity and storage instability.

We have developed a new type of color dosimeter based on the radiation-induced coloration of photochromic compounds. Thermally reversible photochromic compounds, such as spirobenzopyran or azobenzene derivatives, can not be used in this dosimeter because the color disappears even in the dark. Only

thermally irreversible photochromic compounds, such as diarylethenes with heterocyclic aryl groups, can be used in this dosimeter because the colored state remains stable after irradiation and never returns to the colorless state. So far, we have reported on radiation-induced coloration of diarylethenes in the single crystalline phase in solutions and in polymer films.^{6–9} The addition of sensitizers, which have higher excited energies than diarylethenes, was found to be effective in increasing the radiation sensitivity.

In this study, we report on the radiation-induced coloration of five amorphous diarylethene films (Scheme 1). The bulk amorphous films have the following advantages in color dosimeters. The thin films are composed of an extremely high concentration of the compounds and can be readily prepared by spin-coating. In these high concentration films, high energy radiation is effectively used for coloration without loss of energy



Scheme 1.

during energy migration or transfer, as observed in polymer films containing small amounts of the compounds.

Experimental

The synthesis procedure of the five dithienylethenes was previously described in detail.^{10–15} The bulk amorphous films were prepared by spin-coating of the toluene solutions containing the photochromic compounds or heating the compounds above glass transition temperatures or the melting points using a hot stage (Mettler FP 80 Type). The films were irradiated with Co-60 γ -rays at room temperature. The thickness of the amorphous films was measured using a Tencor profilometer (Alpha-step 500). The absorption spectrum was measured with a Shimadzu UV-3100PC spectrometer.

Results and Discussion

The radiation sensitivity of the five amorphous diarylethenes was studied. Diarylethenes **1–4** form an inherently stable amorphous state, with the glass transition temperatures (T_g) reported to be 82 °C, 127 °C, 102 °C, and 68 °C, respectively.^{10–15} On the other hand, compound **5** is essentially crystalline and forms an unstable amorphous state after rapidly cooling the melted liquid. Bulk amorphous films were prepared by spin-coating the toluene solutions (**1**, **2**, and **3**) or by heating the crystalline diarylethenes (**4** and **5**).

Diarylethenes **2–4** form microcrystals when carefully recrystallized from hexane solutions. In the crystalline state, radiation-induced coloration was hardly observed. Even using 10000 Gy, microcrystals **2** and **4** only slightly changed color,

from colorless to a faint red and a pale blue, respectively. The color change in microcrystal **3** was negligible. Crystalline **5** did not show any coloration upon γ -irradiation. On the other hand, radiation-induced coloration of diarylethenes **2–5** was observed in the amorphous state upon 1000 Gy irradiation.

We studied the radiation-induced coloration of compound **1** in detail in the amorphous state. Figure 1 shows the absorption spectra of the bulk amorphous film of **1** (film thickness: 130 μm) irradiated at 2000 Gy. Before γ -irradiation, the amorphous film is colorless. Upon γ -irradiation, the amorphous film turned blue, with an absorption maximum at 570 nm. The color change suggests that γ -irradiation induces a cyclization reaction of the open-ring isomer **1a** to the closed-ring isomer **1b** (Scheme 2). The color change could be detected even at 300 Gy and reached the limit of absorbance measurement at 3000 Gy. Upon photoirradiation with visible light ($\lambda > 450 \text{ nm}$) the color disappeared.

For the color dosimeter application, it is indispensable for the film to show a linear relationship between the absorbed dose and the radiation-induced coloration intensity. Figure 2 shows the dose dependence curve of the bulk amorphous films of **1**. The coloration increases linearly with an increase in the radiation dose. The coloration was found to be linear with the radiation dose up to 3000 Gy. The film could be reused after bleaching the color with visible light ($\lambda > 450 \text{ nm}$). The sensitivity remained at 80% of the initial value even after 10 cycles (500 Gy \times 10).

As described before, compound **5** is obtained as a microcrystalline powder. Upon melting and cooling at room temperature, compound **5** formed a glassy amorphous film. The glass transition temperature was observed at 18 °C in the DSC curve. The

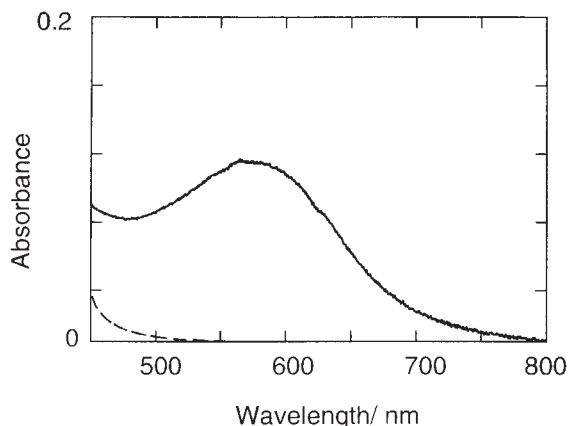


Fig. 1. Absorption spectra of bulk amorphous films **1a**. Bold line: after γ -irradiation. Broken line: before γ -irradiation. Film thickness: 130 μm . Irradiation dose: 2000 Gy.

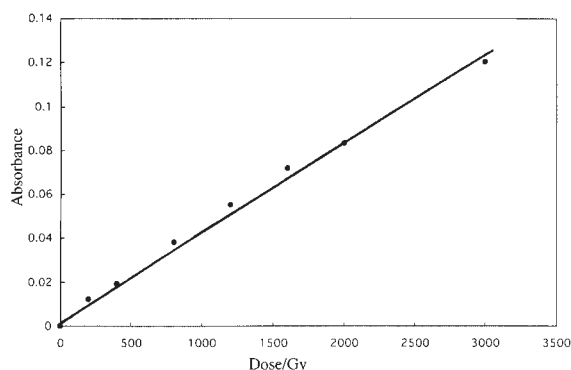
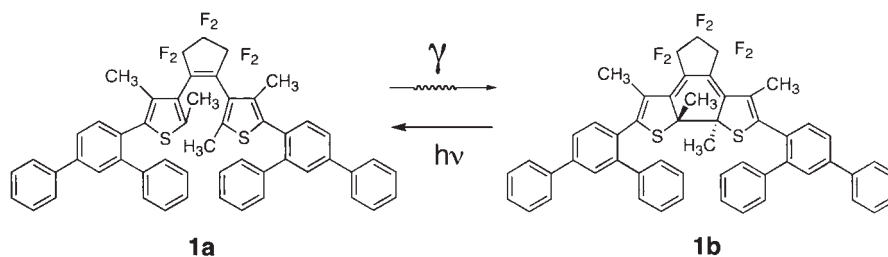


Fig. 2. Dose response curve of the radiation-induced coloration of bulk amorphous films **1a**. Film thickness: 130 μm . Irradiation dose rate: 100 Gy/h.



Scheme 2.

colorless film was irradiated. Figure 3 shows the spectrum of the red color of the amorphous film **5** irradiated to a dose of 1000 Gy. The broken line in Fig. 3 is the absorption spectrum before irradiation. The absorption band at 530 nm is due to the closed-ring isomer **5b**, as shown below (Scheme 3). Upon γ -irradiation, the open-ring isomer **5a** converts to the red-colored closed-ring isomer **5b**.

The dose dependence was also measured for the amorphous film of **5**, as shown in Fig. 4. The absorption intensity increased linearly with an increase in the radiation dose. This linear relationship indicates that the amorphous film can be applied to a color dosimeter.

Table 1 summarizes the radiation-induced coloration of the five diarylethene derivatives in the bulk amorphous state irradiated at 500 Gy. The film thickness, measured by a Tencor profilometer, is also shown in Table 1. The sensitivity of the radiation-induced coloration of the amorphous film **1** is the highest among the derivatives. The sensitivity of the film of **2** is the lowest.

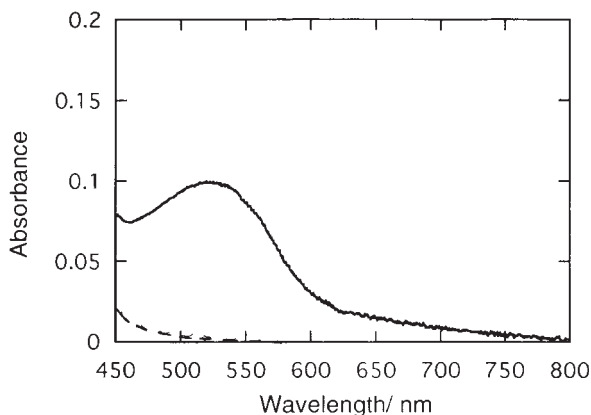
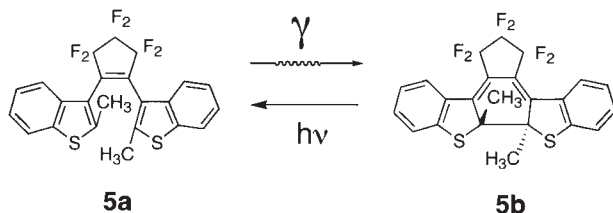


Fig. 3. Absorption spectra of bulk amorphous films **5a**. Bold line: after γ -irradiation. Broken line: before γ -irradiation. Film thickness: 110 μm . Irradiation dose: 3000 Gy.



Scheme 3.

Excitation to high energy excited states of diarylethenes by γ -irradiation is considered to be responsible for the radiation-induced coloration of the amorphous films. The excited states degrade to the lowest excited states of the diarylethenes, and the open-ring isomers convert to the colored closed-ring isomers, as is normally observed in photochromic reactions. According to this mechanism, the radiation sensitivity should be in good correlation with the sensitivity of the photo-induced coloration of the derivatives. To test this correlation, we measured the relative coloration rate of the amorphous films of the five derivatives.

Figure 5 shows the photo-induced coloration of the five de-

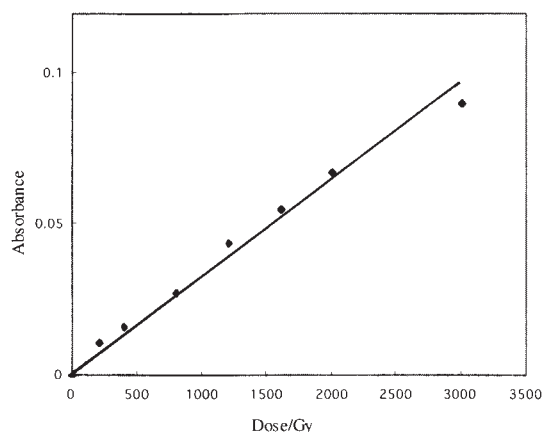


Fig. 4. Dose response curve of the radiation-induced coloration of bulk amorphous films **5a**. Film thickness: 110 μm . Irradiation dose rate: 100 Gy/h.

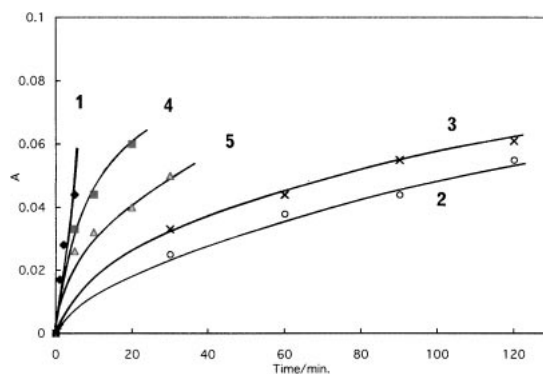


Fig. 5. Photo-induced coloration of bulk amorphous diarylethenes **1–5** shown in Scheme 1. The film thickness: **1**: 70 μm , **4**: 80 μm , **5**: 80 μm , **3**: 80 μm , **2**: 80 μm .

Table 1. Radiation Sensitivity of Amorphous DAE Films

DAE	Film thickness/ μm	Absorbance ^{a)}	Relative sensitivity (Normalized at 130 μm)	Relative photo-coloration rate ^{b)}
1	130	0.033	1.00	1.00
2	110	0.010	0.33	0.15
3	130	0.012	0.36	0.23
4	90	0.018	0.79	0.67
5	110	0.020	0.67	0.54

a) Total dose 500 Gy. b) Upon irradiation with 254 nm light.

rivatives in bulk amorphous films upon irradiation with 254 nm light. The films are thick enough to absorb all irradiated photons. The intensity of the color increases with an increase in the irradiation time until saturation. The most sensitive amorphous film is **1**. The efficiency of the photo-induced coloration of **2** is the lowest. The relative sensitivities derived from the initial slopes are also summarized in Table 1. Although the relative photo-sensitivities qualitatively agree with the radiation sensitivities, the absolute ratios are different. This difference suggests that not only the lowest excited states but also higher excited states contribute to the production of the colored isomers. There exist channels in the higher excited states in which the open-ring isomers convert to the closed-ring isomers.

These amorphous film color dosimeters showed excellent storage stability. The radiation-induced color did not change in the dark at room temperature for more than a year.

Conclusion

The radiation sensitivity of the bulk amorphous films of five photochromic diarylethenes was studied with the aim of developing reusable, sensitive color dosimeters. Although radiation-induced coloration was scarcely observed in the single crystalline state, effective coloration of the amorphous films was observed upon γ -irradiation. The color disappeared upon visible photoirradiation. The coloration increased linearly with an increase in the absorbed dose. Although the relative coloration sensitivity qualitatively agreed with the sensitivity of the photo-induced coloration, the absolute ratios were different. This result suggests that the high energy radiation excites the open-ring isomers to higher excited states, and the excited

open-ring isomers convert to closed-ring isomers in both the lowest excited states as well as in the higher excited states.

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