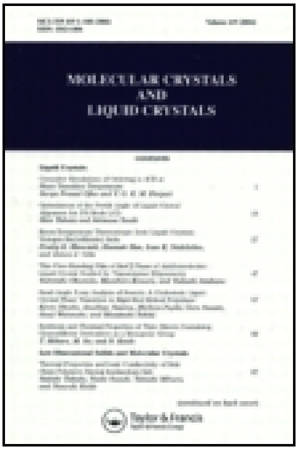

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Radiation Sensitivity of Photochromic Diarylethenes

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Radiation Sensitivity of Photochromic Diarylethenes

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The radiation sensitivity of photochromic dithienylethenes was studied with the aim of developing a new reusable color film dosimeter. Upon γ-irradiation, polystyrene films containing 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **1** and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **2** turned red and blue, respectively. The red and blue colors disappeared by visible-light irradiation and the films could be reused. In both films the absorption intensities of the colors linearly increased with the absorbed dose. From the color change it was possible to estimate the radiation dose.

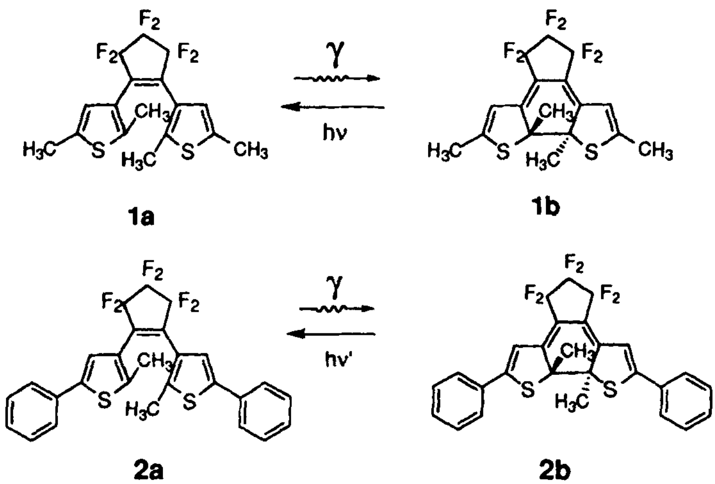
Keywords: Diarylethenes; Radiation; Sensitivity

INTRODUCTION

Various type of dosimeters have been developed. Among them chemical color dosimeter, which is based on color change of dyes by radiation-induced chemical reactions, are the most convenient and frequently used for radiation sterilization of biomedical materials.[1] So far acids or radicals, which are produced by radiation, trigger the coloration of dyes. A typical example is vinylchloride-vinylacetate copolymer film containing methyl orange.[2]

In a previous paper, we have reported that photochromic diarylethenes can be used as reusable chemical color dosimeters. Single crystalline diarylethenes and benzene solutions containing diarylethenes changed the color upon γ-irradiation and the color disappeared by visible light irradiation (Scheme 1).[3] The reason why diarylethenes with heterocyclic aryl groups, such as furan or thiophene rings, can be used as dosimeters is that the colored isomers are thermally stable and never return to the colorless forms in the dark.[4,5] Thermally reversible photochromic compounds, such as spirobenzopyrans, can not be used as the dosimeters, because the color is bleached thermally even in the dark and linear dose dependence of the coloration is not attained.

In the present study we attempted to develop a new high sensitive film dosimeter using the diarylethenes. We have examined the radiation sensitivity of two dithienylethenes, 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1**) and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2**) in various polymer films to know the feasibility. The photochromic film dosimeter is advantageous over present chemical dosimeters in the sensitivity and the reusable characteristic.



Scheme 1

RESULTS AND DISCUSSION

For the practical application it is desired to develop film dosimeters. A convenient way to prepare such film dosimeters is to disperse photochromic diarylethenes in polymer films. In the present study, we have investigated the radiation induced coloration of **1a** and **2a** in various polymer matrices to search for suitable polymers.

A self-standing polystyrene film containing 2 wt% of **1a** was prepared by casting a toluene solution containing polystyrene and **1a** on a Teflon plastic plate (the film thickness ~ ca 0.75 mm) and irradiated with Co-60 γ-rays (dose rate = 100 Gy/hr) for 20 hrs (total dose 2.0 kGy). Before irradiation the film was colorless. Upon γ-irradiation the film turned red and the absorption maximum was observed at 530 nm, which is the same as that of the closed-ring form produced by ultraviolet irradiation, as shown in Figure 1. This indicates that the cyclization reaction of **1a** to the closed-ring form **1b** took place by γ-irradiation in the polystyrene film. The red film became again colorless upon irradiation with visible light irradiation.

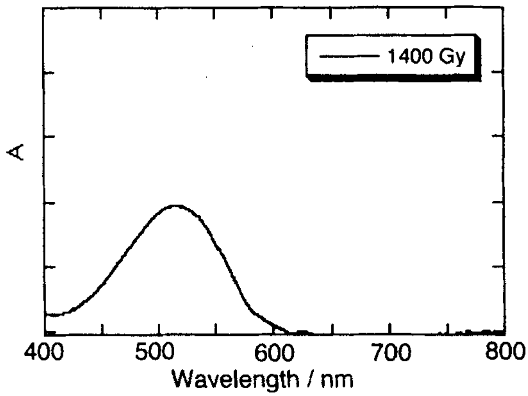


Figure 1. Absorption spectrum of a polystyrene film of 1 γ-irradiated with a dose of 10 kGy. Before γ-irradiation the film had no absorption longer than 400 nm. The thickness of the film was 0.75 mm.

The radiation-induced coloration efficiency was dependent on the polymer matrices used. The matrix dependence of the efficiency was examined using thin polymer films (film thickness ~ 0.2 mm), as shown in Table 1. When poly(methylmethacrylate) (PMMA) was used as the matrix, the coloration was scarcely observed. The absorbance after irradiation of 1 kGy was only 0.01. The coloration in poly(N-vinylcarbazole) was also inefficient and similar to the coloration in PMMA. On the other hand, rather efficient coloration was observed in polycarbonate, but the efficiency was 0.67 of that in polystyrene.

Table 1

Radiation-Induced Coloration of 1 in Polymer Matrix

Polymer	A	
Polystyrene	0.033	(1.00)
PMMA	0.010	(0.30)
Amorphous polyolefin	0.016	(0.48)
Polycarbonate	0.022	(0.67)
Poly(N-vinylcarbazole)	0.018	(0.55)

Total dose: 1000 Gy, Film thickness: 0.2 mm

Linear dose dependence of the coloration is indispensable for the practical application. When the absorption intensity of the color increases in proportion to the absorbed dose, the absorbed dose can be estimated from the absorbance. Figure 2 shows the dose dependence of the absorbance at 530 nm of polystyrene film containing 2 wt% of 1 (the film thickness = 0.75 mm).

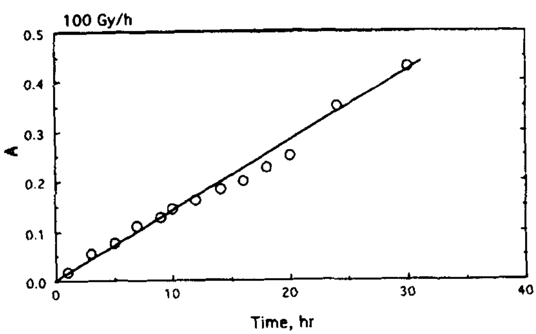


Figure 2. Dose response curve of polystyrene film of **1**. Dose rate was 100 Gy/hr. The thickness of the film was 0.75 mm.

The absorbance linearly increased until the absorbed dose of 3 kGy. The linear dependence was also observed for the reused films, so far the total irradiated dose was less than 50 kGy. Above 100 kGy the film started to decompose.

One of the advantage of the diarylethane dosimeter is that any kinds of color can be obtained just by changing the substituents. A polystyrene film containing **2a** was irradiated with γ-rays and the color change was examined. In this system the color changed from colorless to blue. The radiation-induced coloration efficiency was also dependent on the polymer matrices used. When poly(methylmethacrylate) (PMMA) was used as the matrix, the coloration was scarcely observed. The absorbance after irradiation of 1 kGy was only 0.017. The coloration in poly(N-vinylcarbazole) was also inefficient and similar to the coloration in PMMA. On the other hand, rather efficient coloration was observed in polycarbonate, but the efficiency was half of that in polystyrene. Excitation energy transfer from polymers to dithienylethenes is considered to play a role in the coloration process in the polymer films.

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