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Radiation-Induced Coloration of Photochromic Dithienylethene Derivatives in Polymer Matrices

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The high-energy radiation-induced coloration of photochromic dithienylethenes was studied in various polymer matrices with the aim of developing a reusable color plastic dosimeter. Upon γ-irradiation, polystyrene films containing 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **1a** and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **2a** turned red and blue, respectively. The red and blue colors disappeared upon irradiation with visible light, and the films could be reused. In both films the absorption intensities of the colors increased linearly with the absorbed dose. Although radiation-induced coloration was clearly detected in polystyrene films, a color change was scarcely observed in poly(methyl methacrylate) (PMMA) and poly(*N*-vinyl carbazole) containing **1a** and **2a**. Excitation energy transfer from polymers to dithienylethenes is considered to play a role in the coloration process in polymer films.

Various type of dosimeters have been developed.[1] Among them, a chemical color dosimeter based on the color change of dyes by radiation-induced chemical reactions are the most convenient and frequently used for radiation sterilization.[2] So far, acids or radicals, which are produced by radiation, trigger the coloration of dyes. A typical example is a vinyl chloride–vinyl acetate copolymer film containing Methyl Yellow, in which radiation-generated acids change the color of the dye from yellow to red.[3]

In a previous paper,[4] we reported that the single crystalline 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **1a** and benzene solutions containing **1a** changed the color from colorless to red upon γ-irradiation, and that the color disappeared upon visible-light irradiation. In these systems, the coloration is due to radiation-induced excitation of the diarylethenes. The reason why diarylethenes with heterocyclic aryl groups can be used as dosimeters is that the colored isomers are thermally stable and never return to the colorless forms in the dark.[5] Thermally reversible photochromic compounds, such as spirobenzopyrans or azobenzene, can not be used as dosimeters, because the color is thermally bleached, even in the dark, and a linear dose dependence of the coloration, which is indispensable to the dosimeters, is not attained.

For practical applications it is required to develop film dosimeters. A convenient way to prepare these is to disperse photochromic diarylethenes in polymer films. In the present study, we investigated the radiation induced coloration of 1, 2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **2a** and **1a** in various polymer matrices and searched for suitable polymer matrices for reusable color dosimeters.

Experimental

The details of synthetic procedures of dithienylethene derivatives **1** and **2** have been reported elsewhere.[6,7] Polystyrene (M_w = 95000), poly(methyl methacrylate) (PMMA) (M_w = 100000), polycarbonate (M_w = 25000) and poly(*N*-vinyl carbazole) (M_w = 80000) were used as polymer matrices. The polymers were purchased from Chemco, and GL. Sciences Ltd. Polymer films containing dithienylethene derivatives were prepared by casting toluene solutions containing polymers and dithienylethene derivatives on a Teflon® plastic plate. The films were dried under a vacuum, and then irradiated with Co-60 γ-rays at room temperature. The thickness of the polymer films was measured by a micrometer (Mitsutoyo Co. Model C-112). The absorption spectra in polymers were measured with an absorption spectrophotometer (Shimadzu UV-3100PC).

Results and Discussion

A self-standing polystyrene film (the film thickness: ca. 0.75 mm) containing 2.0 wt% of **2a** was prepared by casting a portion of a toluene (8 ml) solution containing polystyrene (2 g) and **2a** (40 mg) on a Teflon® plastic plate. The film was dried under vacuum and then irradiated with Co-60 γ-rays (dose rate = 100 Gy h^{-1}) for 20 h (total dose 2.0 kGy). Before irradiation, the film was colorless. Upon γ-irradiation, the film turned blue and the absorption maximum was observed at 605 nm, which is the same as that of the closed-ring isomer **2b** produced by ultraviolet irradiation, as shown in Fig. 1. This indicates that the cyclization reaction of **2a** to the closed-ring isomer **2b** took place by γ-irradiation in the polystyrene

CREST, Japan Science and Technology Corporation.

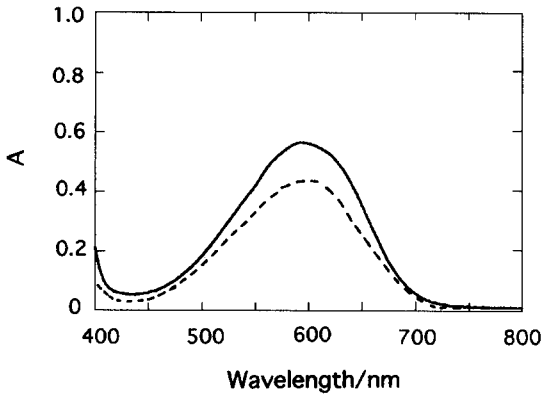


Fig. 1. Absorption spectra of polystyrene film containing **2a** (2.0 wt%) irradiated (—) with a total dose of 2.0 kGy and (- - -) with 313 nm light. The film thickness was 0.75 mm. Before γ-irradiation the film had no absorption longer than 400 nm.

film (Chart 1.). The blue film returned to colorless upon irradiation with visible light. The coloration by γ-irradiation and bleaching by visible light could be repeated more than 10 times without any loss of performance.

The radiation-induced coloration efficiency was dependent on the polymer matrices used, as shown in Table 1. Efficient coloration was observed in a polystyrene film, while coloration was scarcely observed in a poly(methyl methacrylate) (PMMA) film. The absorbance after irradiation of 1 kGy was only 0.017 (the content of **2a**: 2.0 wt%, the film thickness: ca. 0.20 mm). The coloration in a poly(*N*-vinyl carbazole) film was also inefficient and similar to that in the PMMA film. On the other hand, rather efficient coloration

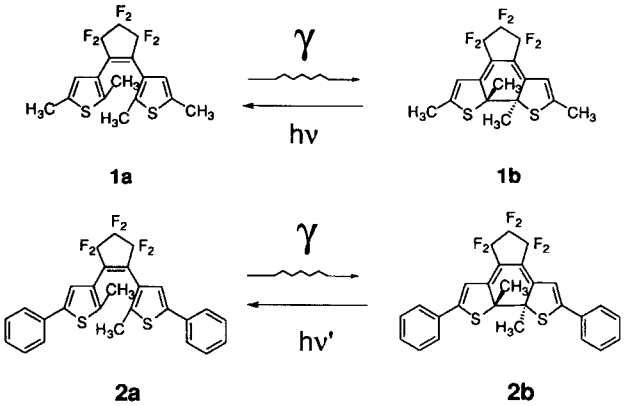


Chart 1.

Table 1. Radiation-Induced Coloration of **2** in Polymer Matrices[a)]

Polymer	Absorbance	
Polystyrene	0.078	(1.00)[b)]
PMMA	0.017	(0.22)
Polycarbonate	0.033	(0.42)
Poly(*N*-vinylcarbazole)	0.018	(0.23)

a) Total dose: 1000 Gy, Content of **2a**: 2.0 wt%, Film thickness: 0.20 mm. b) Relative values were shown in parenthesis.

was observed in a polycarbonate film, but the efficiency was less than half that in the polystyrene film.

A linear dose dependence of the coloration is indispensable for practical applications. 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 605 nm. In this experiment the polystyrene film contained 2.0 wt% of **2a** and the film thickness was 0.75 mm. The absorbance increased linearly below an absorbed dose of 3 kGy. Below 3 kGy, decoloration by the radiation was negligible because of the low concentration of the radiation-generated colored isomers. A linear dependence was also observed for reused films, as long as the total irradiated dose was less than 50 kGy. Above 100 kGy the film started to decompose.

Figure 3 shows photographs of the color changes of polystyrene films (the content of **2a**: 2.0 wt%, the film thickness: ca. 0.75 mm) irradiated with γ-rays. As can be seen from Fig. 3, the blue color of the film became deeper with an increase in the irradiated dose (or absorbed dose). Even if the absorbed dose was as small as 100 Gy, a clear color change was observed. It is worthwhile to note that the absorption intensity of the color linearly increased with the film thickness. When the thickness was as large as 7.5 mm, the color change induced by a dose of 100 Gy was the same as that observed at a dose of 1 kGy of Fig. 3. It is possible to increase the sensitivity just by increasing the film thickness.

The coloration efficiency was also dependent on the content of **2a** in the polymer film. Figure 4a shows the concentration dependence in polystyrene film. The coloration efficiency was almost saturated at a content of 25 wt%. From the saturation curve, it is possible to estimate the energy transfer distance using a modified Perrin equation:[8]

$$\ln\left(\frac{\Phi_\infty}{\Phi_\infty - \Phi_D}\right) = VN[Q],$$

$$V = (4/3\pi)R_0^3,$$

where Φ_∞ and Φ_D are the absorption intensities at infinite concentration of **2a** and at given concentrations, respectively. N, $[Q]$, V, and R_0 are Avogadro's number, the concentration of **2a**, the reaction volume and the energy transfer dis-

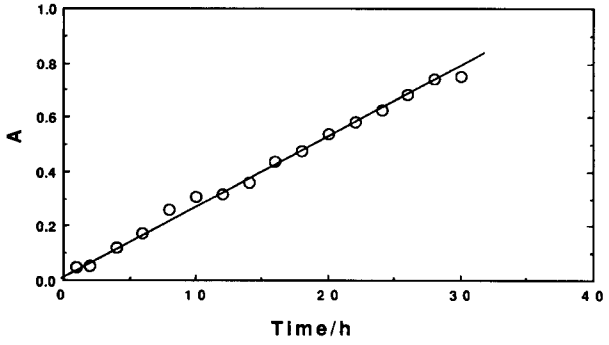
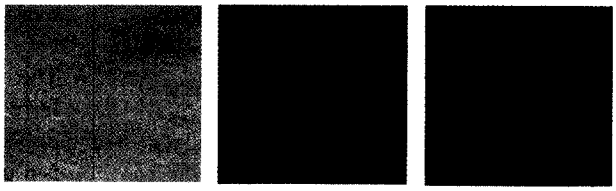


Fig. 2. Dose response curve of a polystyrene film containing **2a** (2.0 wt%). Dose rate was 100 Gy h^{-1}. The film thickness was 0.75 mm.



	0 Gy	100 Gy	500 Gy	1000 Gy	3000 Gy
A		0.035	0.175	0.35	0.9

Fig. 3. Photos of polystyrene films containing **2** (2.0 wt%) irradiated with γ-rays. The film thickness was 0.75 mm.

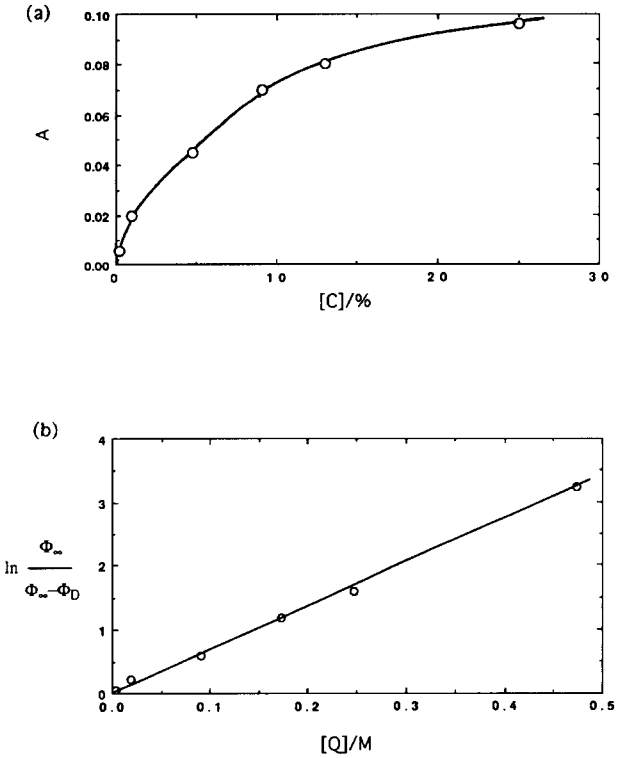


Fig. 4. (a) Concentration dependence of coloration of **2** in polystyrene film. Total dose was 1 kGy. The film thickness was 0.20 mm. (b) Modified Perrin plots (see the details in the text).

tance, respectively. The estimated distance from the plots shown in Fig. 4b is 14 Å, which indicates that excited energy is transferred from the polymer to dithienylethenes by a dipole–dipole interaction mechanism.

One of the advantages of the diarylethene dosimeter is that any kinds of color can be obtained by just changing the substituents. A polystyrene film containing **1a** was irradiated with γ-rays and the color change was examined. Figure 5 shows photographs of the color changes of films containing **1a**. In this system the color changed from colorless to red. Figure 6 shows the dose dependence of the coloration. The intensity of the absorbance at 520 nm increased linearly with the irradiated dose until 3 kGy. The linear dependence indicates that the film can also be used as a color dosimeter.

Based on the above results, the mechanism of the radiation-induced coloration in polymer films is considered to be as shown in Chart 2. First, the polymer absorbs energy by γ-rays irradiation, and various types of higher excited states are produced in the polymer matrix. The higher excited states are relaxed to the most stable excited singlet states of the phenyl side groups in the polystyrene film. When a doped dithienylethene exists close to the excited

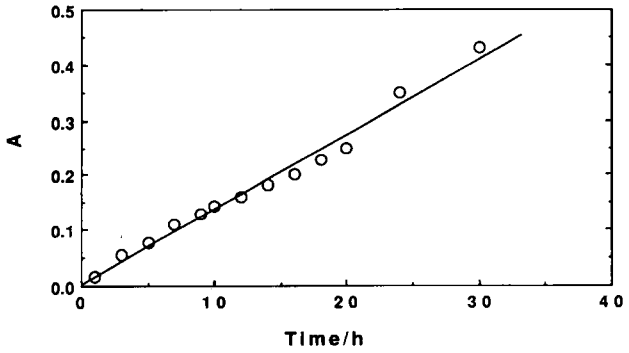
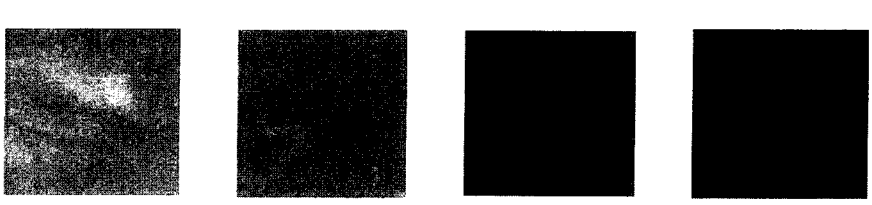


Fig. 6. Dose response curve of polystyrene films containing **1a** (2.0 wt%) irradiated with γ-rays. Dose rate was 100 Gy h^{-1}. The film thickness was 0.75 mm.



	0 Gy	500 Gy	1000 Gy	2000 Gy	3000 Gy
A		0.075	0.15	0.25	0.43

Fig. 5. Photos of polystyrene films containing **1** (2.0 wt%) irradiated with γ-rays. The film thickness was 0.75 mm.

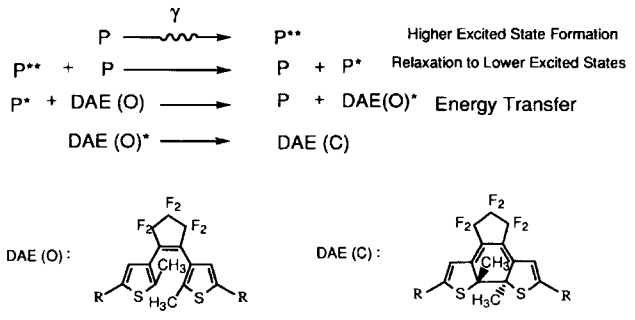


Chart 2.

phenyl side groups, the excited energy is transferred to the dithienylethene molecule and an excited dithienylethene is produced. The energy transfer distance was estimated to be 14 Å from the concentration dependence of the coloration (Fig. 4a). The excited dithienylethene converts to a closed-ring isomer with a certain probability, and coloration of the film takes place. This is a probable mechanism of radiation-induced coloration.

According to the above mechanism, the energy level of the most stable excited state of the polymer matrix plays an important role in the coloration process. When the excited singlet state energy level is higher than the first excited singlet state of the doped dithienylethene, the excited energy of the matrix can be transferred to the dithienylethene and coloration takes place. On the other hand, when the energy level is lower than the excited state energy level of the dithienylethene, the excited energy cannot be transferred to the dyes. The weak coloration in a poly(*N*-vinyl carbazole) film is explained by this mechanism. The excited singlet energy level of carbazole is lower than that of **2a**.[9] The intermediate coloration of polycarbonate film is ascribed to the presence of substituted phenyl groups in the main chain.

The lifetime of the excited singlet states of polymer matrices also plays a role in the efficiency of energy transfer, because the triplet states of dithienylethene are not responsible to the coloration reactions.[10] When the lifetime is too short, the energy transfer efficiency is decreased. PMMA has aliphatic carbonyl groups. The excited singlet state in PMMA efficiently interconverts to the triplet state, and the lifetime of the excited singlet state becomes short. This is the reason why the coloration efficiency in the PMMA film was very low. Polycarbonate has phenyl and carbonyl groups. The excited singlet states of the phenyl groups can be transferred to the dithienylethenes, but the efficiency is in between polystyrene and PMMA. The radiation-induced coloration is a useful method to study the energy transfer processes in polymer matrices.

Summary

We have examined the radiation-induced coloration of 1, 2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **2a** and 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **1a** in various polymer matrices. Although an efficient coloration of the diarylethenes was detected in polystyrene films, the coloration was scarcely observed in poly(*N*-vinyl carbazole) and PMMA. The absorption intensity of the color of the polystyrene films increased linearly with the irradiated dose below 3 kGy. The linear dependence indicates the possible application of a polystyrene film containing dithienylethenes to sensitive reusable color dosimeters.

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