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The Effect of Additives on the Radiation-Induced Coloration of Photochromic Dithienylethene Derivatives

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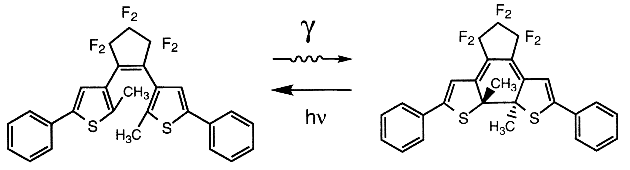
The effect of the addition of metal complexes and aromatic compounds on the radiation-induced coloration of polystyrene films containing 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene was examined to develop a sensitive reusable color plastic dosimeter. By the addition of metal complexes, the radiation sensitivity increased along with an increase in the atomic numbers. When aromatic compounds, such as naphthalene, biphenyl, and acenaphthene, were added to the polymer film, the coloration sensitivity increased, while the addition of anthracene and pyrene decreased the sensitivity. Excitation energy transfer from the sensitizers to the dithienylethene is considered to play an important role in the radiation-induced coloration in polystyrene films containing the additives.

Medical articles, such as blood and some tubes of dialysis, are widely sterilized by irradiation with γ-rays. For such a treatment it is strongly desired to develop convenient and sensitive dosimeters.[1] One of the candidates is a plastic color dosimeter. The color dosimeter can estimate the dose from a color change or an intensity change of the color. The chemical dosimeter so far developed was based on a color change induced by reactions triggered by radiation-generated acids or radicals.[2,3] Although they are widely used, the deficiency is low sensitivity.

Previously, we reported on a color plastic dosimeter based on the radiation-induced coloration of photochromic dithienylethene derivatives.[4–6] The coloration is due to the radiation-induced excitation of diarylethenes. The reason why diarylethenes can be used as a dosimeter is that the colored isomers are thermally stable and never return to colorless isomers in the dark. We used 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **1a** (Chart 1) because of the thermal stability of the colored isomer (the half lifetime: 1900 years at 30 °C).[7] Thermally reversible photochromic compounds, such as spirobenzopyrans or azobenzene, can not be used as a dosimeter, because the color is thermally bleached even in the dark.

In this work, we studied the additive effect on the radiation-induced coloration of polystyrene films containing 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **1a** in aiming at increasing the radiation sensitivity. We examined the addition of metal complexes, which increase the absorbed dose, and aromatic compounds, which can transfer the excited energy to the dithienylethene.



1a 1b

Chart 1.

Experimental

The synthesis of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **1a** was reported previously.[8] Toluene solutions containing polystyrene **1a** and additives were casted on a Teflon plastic plate. The films were dried under a vacuum, and then irradiated with Co-60 γ-rays at room temperature. Metal complexes, such as ferrocene [$Fe(C_5H_5)_2$], hexacarbonylmolybdenum [$Mo(CO)_6$], dodecacarbonyltriruthenium [$Ru_3(CO)_{12}$], hexacarbonyltungsten [$W(CO)_6$], decacarbonyldirhenium [$Re_2(CO)_{10}$], and aromatic compounds, such as naphthalene, biphenyl, acenaphthene, anthracene, and pyrene, were used as additives. The thickness of the polymer films was measured by a micrometer (Mitsutoyo co. Model C-112). The absorption and fluorescence spectra were measured with a Shimadzu UV-3100PC spectrometer and a RF-5000 fluorometer.

Results and Discussion

1. The Addition of Metal Complexes. It is generally accepted that the absorption dose of the γ-ray energy is dependent on the electron density of the materials.[9] If γ-rays or X-rays interact with electrons in atomic or molecular orbitals, three processes are possible: the photoelectronic effect, the Compton effect, and pair formation. Their relative importance depends on the photon energy and the atomic number of the nuclei as well as on the electron density of the irradiated system. In all three cases secondary electrons are ejected, which usually possess sufficient kinetic energy to induce additional

Table 1. Additive Effect on Radiation-Induced Coloration

Additives		Atomic number	Absorbance at 600 nm (relative intensity)
None			0.070 (1.0)
Ferrocene	$[Fe(C_5H_5)_2]$	26	0.070 (1.0)
Hexacarbonylmolybdenum	$[Mo(CO)_6]$	42	0.10 (1.4)
Dodecacarbonyltriruthenium	$[Ru_3(CO)_{12}]$	44	0.13 (1.9)
Hexacarbonyltungsten	$[W(CO)_6]$	74	0.14 (2.0)
Decacarbonyldirhenium	$[Re_2(CO)_{10}]$	75	0.15 (2.2)

Irradiation dose: 1000 Gy. Film thickness: 0.2mm. Content of additives: 0.5 mol/kg.

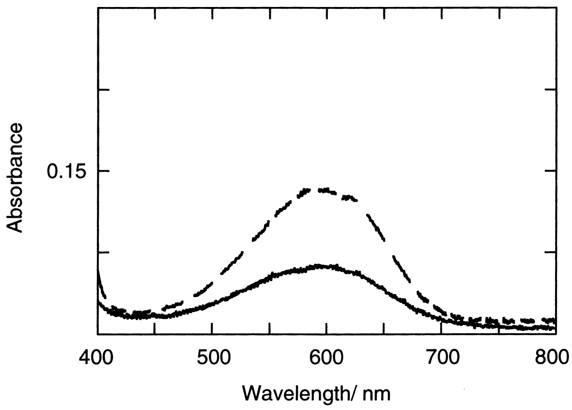


Fig. 1. Absorption spectra of polystyrene films containing **1a**. Bold line: in the absence of decacarbonyldirhenium. Broken line: in the presence of decacarbonyldirhenium (0.41 mol/kg). Irradiation dose: 1000 Gy. Content of **1a**: 8 wt%.

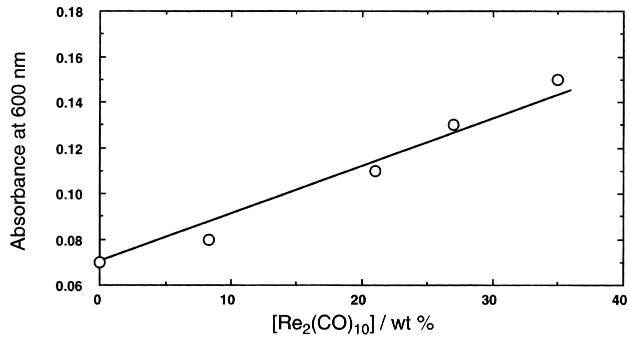


Fig. 2. Concentration dependence of decacarbonyldirhenium on the radiation-induced coloration of polystyrene films containing **1a**. Irradiation dose: 1000 Gy. Content of **1a**: 8 wt%.

ionization or electron excitation in surrounding molecules. The contribution of the Compton process to the total absorption coefficient is entirely dependent on the number of electrons per gram of sample. Therefore, it is expected that the absorbed dose increases by the addition of metal complexes having a large atomic number. We studied the effect of the addition of metal complexes on the radiation-induced coloration of polystyrene films containing diarylethene **1a**.

Figure 1 shows the absorption spectrum of polystyrene films irradiated to a dose of 1000 Gy in the absence and presence of decacarbonyl dirhenium $[Re_2(CO)_{10}]$ (0.41 mol/kg). The absorption intensity increases twice in the presence of a metal complex. Table 1 summarizes the effect of the addition of metal complexes on the radiation-induced coloration of polystyrene films containing diarylethene **1a** (8 wt%). The radiation coloration increased by the addition of the same molar amounts of metal complexes having a large atomic number. These results indicate that the radiation sensitivity can be increased by the addition of a metal complex having a large atomic number. This result is interpreted in terms of the absorption dose increase in the presence of metal complexes.

Figure 2 shows the concentration dependence of decacarbonyl dirhenium on the absorbance of the blue color of the closed-ring isomer **1b**. The coloration increases with increasing the amount of additives. Although the effect of the addition of metal complexes is remarkable, one of the problems is low solubility of the metal complexes in the polymer film. The highest concentration is limited to less than 0.55 mol/kg.

2. The Addition of Aromatic Compounds. In order to further increase the sensitivity, we examined the effect of the addition of aromatic compounds. In a previous report we found that polystyrene film is the most effective film to obtain high sensitivity.[5] Poly(methyl methacrylate) film containing **1a** scarcely changed color upon γ-irradiation. The reason is that the phenyl side groups of the polystyrene act as mediators to capture the radiation energy and to transfer it to the dispersed dithienylethene molecules. Therefore, we examined the effect of the addition of various types of aromatic compounds.

Figure 3 shows the absorption spectrum change of polystyrene films containing **1a** and the same molar amounts of aromatic compounds irradiated to a dose of 1000 Gy. Although the addition of biphenyl increased the intensity of the blue color, the addition of pyrene decreased the intensity. Table 2 summarizes the effect of the addition of various aromatic compounds on radiation-induced coloration.

Figure 4 shows the concentration dependence of naphthalene. The sensitivity increased linearly with increasing the concentration of naphthalene. These results indicate that the radiation sensitivity is improved by the addition of selective aromatic compounds, such as naphthalene, biphenyl, and acenaphthene.

In order to clarify the reason why biphenyl, acenaphthene, and naphthalene can sensitize the radiation-induced coloration and anthracene and pyrene decrease the sensitivity, we measured the absorption spectrum of **1a** and the fluorescence spectra of these compounds. Figure 5 shows the fluorescence spectra of various sensitizers in cyclohexane. The absorption spec-

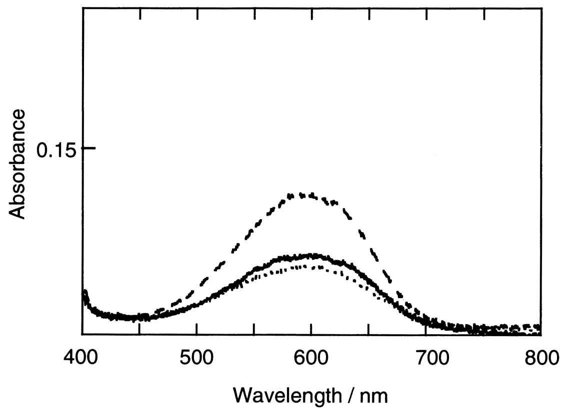


Fig. 3. Absorption spectra of polystyrene films containing **1a**. Bold line: in the absence of aromatic compound. Broken line: in the presence of biphenyl (1.5 mol/kg). Dotted line: in the presence of pyrene (1.5 mol/kg). Irradiation dose: 1000 Gy. Content of **1a**: 8 wt%.

Table 2. Sensitizer Effect on Radiation-Induced Coloration

Additives	Molecular Weights	Absorbance at 600 nm (relative intensity)
None		0.07 (1.0)
Naphthalene	128	0.09 (1.3)
Biphenyl	154	0.12 (1.7)
Acenaphthene	154	0.11 (1.6)
Anthracene	178	0.06 (0.9)
Pyrene	202	0.06 (0.9)

Irradiation dose: 1000 Gy. Film thickness: 0.2 mm. Content of additives: 1.5 mol/kg.

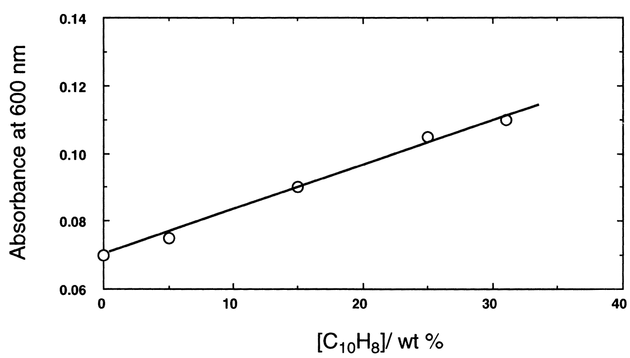


Fig. 4. Concentration dependence of naphthalene on the radiation-induced coloration of polystyrene films containing **1a** (8 wt%). Irradiation dose: 1000 Gy.

trum of **1a** is also shown in Fig. 5. The fluorescence spectra of biphenyl, acenaphthene, and naphthalene overlap with the absorption spectrum of **1a**, while the fluorescence spectra of pyrene and anthracene are shifted to longer wavelengths than that of **1a**. The spectral overlap indicates that the energy level of **1a** is lower than that of the excited states of biphenyl, acenaphthene, and naphthalene, while those of pyrene and anthracene are lower than that of **1a**. In the case of pyrene and anthracene, it is impossible to transfer the energy from them to **1a**. In the case of acenaphthene, naphthalene, and biphenyl,

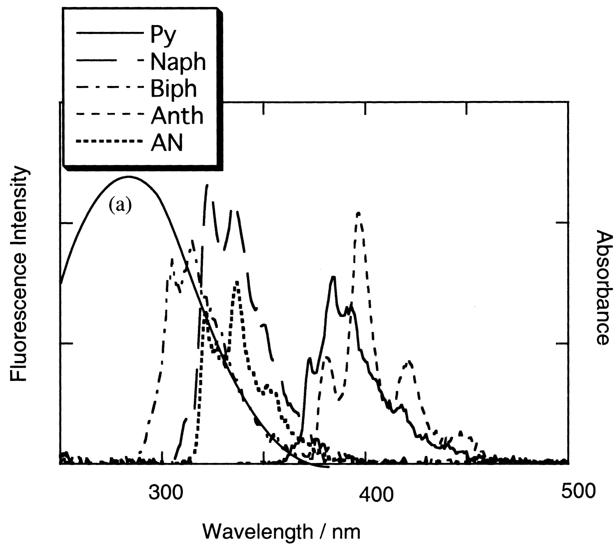
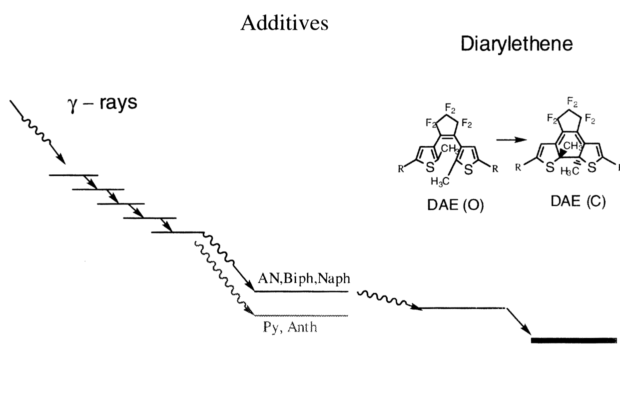


Fig. 5. Absorption spectrum of diarylethene **1a** in cyclohexane ((a) right scale), and fluorescence spectra of naphthalene, pyrene, acenaphthene, biphenyl, and anthracene in cyclohexane (left scale).

the excited energy produced by γ-irradiation can transfer from the aromatic compounds to **1a**. The additive effect is explained by the excited energy transfer.

3. The Addition of both Metal Complex and Aromatic Compound. The above addition effect suggests that the addition of both metal complexes and aromatic compounds further improves the sensitivity. We used decacarbonyldirhenium as a metal complex and naphthalene as an aromatic compound. The absorbance of 0.12 at 600 nm in the presence of 27 wt% decacarbonyldirhenium increased to 0.15 by the addition of 27 wt% of naphthalene. The addition of both decacarbonyldirhenium and naphthalene increased the sensitivity by as much as 2.2 times compared to that in the absence of additives.

Based on the above results, the following Scheme 1 is proposed as a possible mechanism.



Scheme 1.

At first, the absorption of the γ-ray energy is enhanced in the presence of metal complexes. When the atomic number of the metal complex is large, the absorbed dose increases. The absorbed high energy is deactivated by such processes as the photoelectronic effect, the Compton effect, and pair formation, and finally excites the phenyl side groups as well as the added aromatic compounds. The excited aromatic groups transfer the energy to **1a**. When the energy level of the excited aromatic compounds is higher than that of **1a**, energy transfer from the complexes to **1a** takes place. When the energy level of the compounds is lower than that of **1a**, it is impossible to transfer energy to **1a**. As a consequence, the number of excited **1a** decreases and the sensitivity is suppressed. The sensitivity of the radiation-induced coloration increases by choosing appropriate additives, aromatic compounds and metal complexes having a large atomic number metal.

Conclusion

The radiation-induced coloration of polystyrene films containing 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **1a** increased by the addition of a metal complex containing a large atomic number metal and aromatic compounds, whose excited energy level was higher than that of **1a**. When compounds such as naphthalene, biphenyl, and acenaphthene were added to the polymer films, the radiation-induced coloration increased, while the coloration decreased by the addition of pyrene and anthracene.

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