Photochromism of Diarylethenes on Porous Aluminum Oxide: Fatigue Resistance and Redox Potentials of the Photochromes

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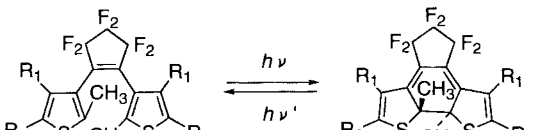
The photochromism of three diarylethene derivatives was examined on porous aluminum oxide. Upon alternate irradiation with UV and visible light, the diarylethenes having thiophene rings decomposed easily, while a derivative having benzothiophene rings underwent a reversible photochromic reaction. The decomposition started from the closed-ring isomers of the dithienylethenes. The decomposition mechanism was discussed based on the oxidation potentials of the compounds.

Photochromic molecules attract much attention from both fundamental as well as practical points of view because of their potential for the application to the optical devices such as optical memories and switches.[1] Among these compounds, diarylethenes are regarded as the best candidate for the application, because of the thermal stability of their both isomers and the fatigue resistant property.[2–5] It is essential for the practical application to study the medium effect on the photochromic reactions.

On the other hand, anodic alumina (Al_2O_3) films, which contain columnar micropores, are an attractive material for use in optical devices.[6] Various optical functions, e.g., spectral selection, polarization, and optical switching, were realized by filling the pores with such guest materials as metal, polymer, and liquid crystal.[7] In this paper, we have examined the photochromic reactions of diarylethenes on the porous alumina film as a solid medium.

Commercially available anodic alumina films (Whatman ANODISC; pore size: 0.2 μm) were used without further treatment. The diarylethenes 1,2-bis(2,5-dimethylthiophen-3-yl)perfluorocyclopentene **(1a)**,[2] 1,2-bis(2,4,5-trimethylthiophen-3-yl)perfluorocyclopentene **(2a)**,[2] and 1,2-bis(2-methylbenzo[*b*]-thiophen-3-yl)perfluorocyclopentene **(3a)**[8] were dissolved in hexane and the films were dipped into the solution and used after drying in vacuo. Absorption spectral changes of the dye on anodic films were observed by reflective spectrometry.



1a: R_1 = H, R_2 = CH_3
2a: R_1 = CH_3, R_2 = CH_3
3a: $\overset{\frown}{R_1, R_2}$ = -CH=CH-CH=CH-

1b: R_1 = H, R_2 = CH_3
2b: R_1 = CH_3, R_2 = CH_3
3b: $\overset{\frown}{R_1, R_2}$ = -CH=CH-CH=CH-

Upon UV irradiation, the films doped with **1–3** turned to red and new bands appeared at 504, 526, and 515 nm, respectively. They are due to the formation of closed-ring isomers **1b**, **2b**, and **3b**. The red color was bleached upon visible light (>500 nm) irradiation and regenerated the open-ring isomers **1a**, **2a**, and **3a**. The coloration–decoloration cycles of the films doped with **1** and **2** were poor, while the film contains **3** showed excellent fatigue resistance. In order to know which isomer is responsible for the decomposition on the alumina surface, isolated open and closed-ring isomers were absorbed on the porous alumina films and time-dependence of spectral changes were observed in the dark.

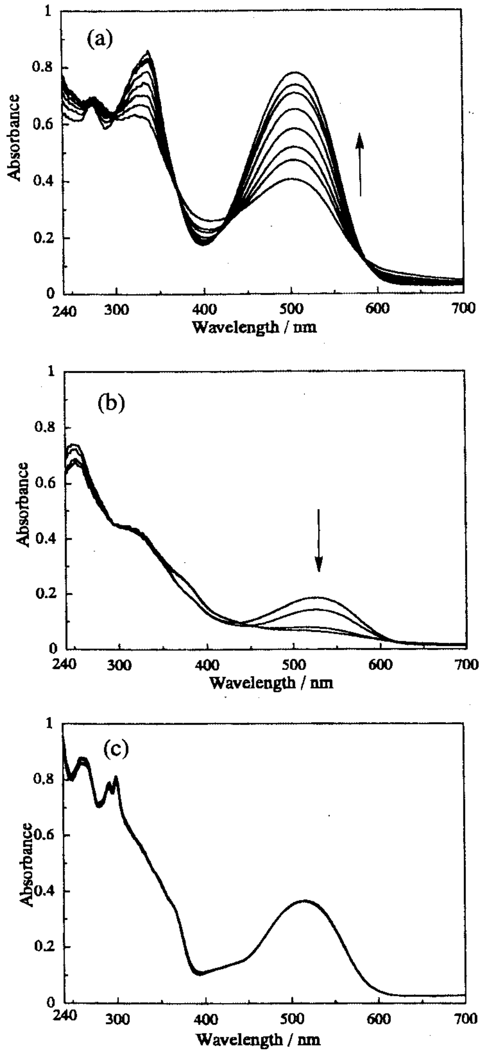


Figure 1. Absorption spectral changes of anodic alumina films doped with diarylethenes **1b** (a), **2b** (b), and **3b** (c) in the dark. Storage time: 0, 1, 2, 4, 8, 16, 24, 48 h for **1b** and **3b**, and 0, 1, 2, 4 h for **2b**.

Absorption spectra of **1a**, **2a**, **3a** and **3b** were stable, while the spectra of **1b** and **2b** were changed on anodic alumina even at room temperature as shown in Figure 1.

In order to know the decomposition mechanism, the oxidation potentials of open- and closed-ring isomers of **1–3** were measured in CH_3CN in a double compartment cell with a standard three-electrode system. The working electrode was in a compartment separated from the rest by sintered glass. Platinum wire and Ag/AgCl (0.1 M tetrabutylammonium chloride in CH_3CN) were used as the counter and reference electrodes, respectively.

The cyclic voltammograms for oxidation of the closed-ring isomers of diarylethenes are shown in Figure 2. Oxidation peaks were observed for **1b** at 0.61 V and **2b** at 0.51 V (vs Ag/Ag^+), while no oxidation peaks were observed for **3b** and all open-ring isomers. These results indicate that the decomposition of the diarylethenes due to the oxidation on anodic alumina film. Diarylethene **3** showed stable photochromism because of its high oxidation potential. We failed to identify the decomposition products by oxidation because of the difficulty to extract the products from the film.

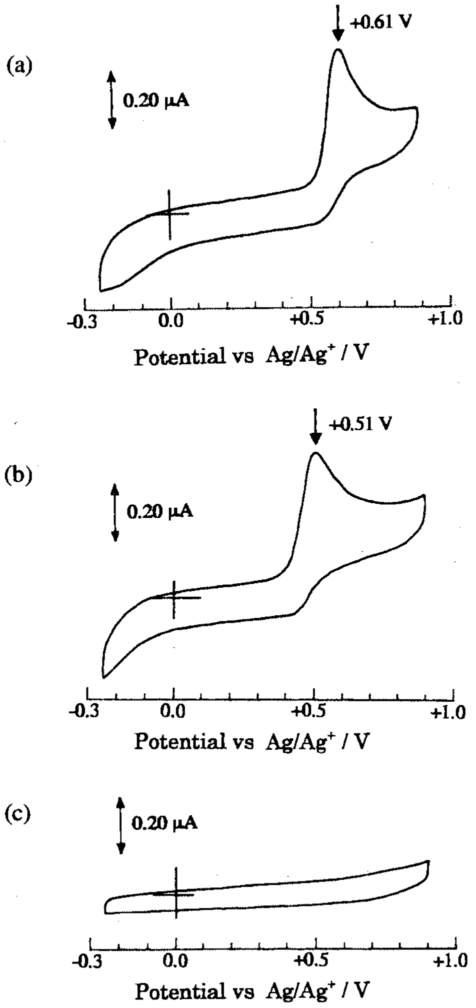


Figure 2. Cyclic voltammograms of the closed-ring isomers **1b** (a), **2b** (b), and **3b** (c) of diarylethenes.

The compound **3** was also introduced into the pores of alumina film by melting. The melting point was 151 °C. Although **3** does not show photochromism in the crystalline phase,[9] the film containing **3** showed a reversible photochromic reaction. This indicates that **3** in the porous film is in the amorphous phase.[10] The amorphous photochromic composite film will be applicable for wave-guide and novel recording media.

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References and Notes

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