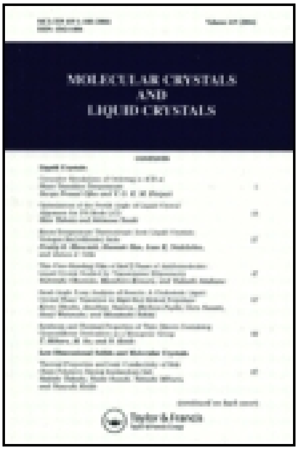

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Photochromic Reaction and Fluorescence of Dithienylethenes in Solid States

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Photochromic Reaction and Fluorescence of Dithienylethenes in Solid States

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Photochromic cyclization reaction efficiency and fluorescence of colloidal solutions, amorphous films, and polymer cast films of two dithienylethenes were studied. Photochromic cyclization reaction efficiency of colloidal solution of cis- 1,2-dicyano- 1,2-dithienylethene (**1**) was as high as that of hexane solution of **1**. Amorphous films of **1** also showed high efficiency. On the other hand, neither colloidal solution nor polycrystal of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**2**) was photochromic; only amorphous films of **2** were colored very slightly by UV irradiation. While photochromic cyclization reaction efficiency of **1** depends little on the kind of polymer matrix, that of **2** depends significantly on the Tg (glass transition temperature) and polarity of polymer matrix. Long-wavelength fluorescence which can be assigned to the colored closed-ring form was observed for **1** in the solid states, though deeply colored hexane solution did not give any long-wavelength fluorescence.

Keywords: 1; 2-diarylethenes; Photochromism; Colloidal solution; Amorphous film; Polymer cast film; Fluorescence

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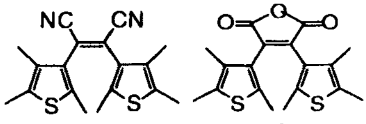
INTRODUCTION

Cis-1,2-diarylethene derivatives have been attracting much attention from the viewpoint of application to photonics devices, because of their high conversion efficiencies of reversible photochromic reactions, excellent thermal stability of both isomers, and good fatigue resistant characteristics [1-7]. If photochromic reactions occur efficiently in solid states, vapor-deposited films or single crystals of photochromic molecules can be used as optical memory media. Some of diarylethenes undergo photochromism in the single crystalline phase [6, 7]. An efficient photochromic reaction of cis-1,2-dicyano-1,2-dithienylethene (**1**) has been reported in amorphous state [8]. Recently, rewritable near-field optical recording has been demonstrated on an amorphous diarylethene film [9].

We have found that colloidal solutions of **1** are photochromic [10]. In the present study, photochromic cyclization reaction efficiency and fluorescence spectra of two dithienylethenes in two neat solid states, colloidal solutions and amorphous films, and also in several polymer matrices, were measured.

EXPERIMENTAL

Dithienylethenes, cis-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (**1**) and 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**2**) were purchased from Tokyo-kasei, Co., and used



1 2

FIGURE 1 Structural formulae of dithienylethenes studied.

without further purification. Figure 1 shows structural formulae of **1** and **2**. Five kinds of polymers, poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(butyl methacrylate) (PBMA), poly(cyclohexyl methacrylate) (PCMA), and poly(bisphenol A carbonate) (PC) were purchased from Aldrich Chemical Co., and three kinds of polymers, PMMA, polystyrene (PS), and poly(vinyl chloride) (PVC) were purchased from Ishizu Co.

Colloidal solutions of dithienylethenes were prepared by pouring a small amount of concentrated methanol solution into pure water at 90 °C. Colloidal solutions of **1** were very stable, while those of **2** were unstable; the latter deposited within a day. The diameter of particles of the colloidal solutions was about 1 μm according to observation by a scanning electron microscope. Amorphous films were made by cooling molten samples between two glass plates [8]. The films were optically isotropic based on observation using a polarizing microscope. Amorphous films of **1** were very stable as reported by Kawai et al. [8], while those of **2** crystallized in several days. Polymer films were obtained by casting mixed chloroform solution of a dithienylethene and a polymer.

Monochromated light from a Xe lamp was used to irradiate the samples. Exciting wavelengths were 330 nm for **1**, and 400 nm for **2**. Relative photochromic cyclization reaction efficiency was calculated from absorbance change in visible region after UV irradiation.

RESULTS AND DISCUSSION

Table 1 summarizes the results for photochromic cyclization reaction efficiencies of colloidal solutions and amorphous films. The coloring efficiency of the colloidal solution of **1** was as high as that of the hexane solution (see Table 1). Colloidal solutions of **2** were not photochromic. The efficiency for the amorphous film of **1** was half of that for the hexane solution. Though neither polycrystal nor colloidal solution of **2** was photochromic, the color of an amorphous film of **2** turned to purple immediately by UV irradiation.

The experimental results for polymer films are summarized in Table 2. **1** shows almost no dependency on kind of polymer matrix. On the other hand, photochromic reaction efficiency and fluorescence wavelength of **2** depend on kind of polymer. The efficiency decreases a little with Tg (glass transition temperature). In other words, hard polymer matrices hinder photochromic reaction of **2**. Fluorescence wavelength can be thought to be a good index of polarity for a polymer matrix; the relationship between photochromic reaction efficiencies vs. wavelengths at fluorescence maxima showed that photochromic reaction efficiency of **2** was very low in a polar polymer matrix. It has been reported that polarity of solvent affects greatly to photochromic reaction of **2** [4].

Though Kawai et al. reported that colored amorphous films of **1** were not fluorescent [8], we observed long-wavelength fluorescence which can be assigned to the colored closed-ring form. Not only colored amorphous films, but also colored colloidal solutions and polymer films of **1** showed long-wavelength fluorescence. On the other hand, we were unable to detect any long-wavelength fluorescence of deeply colored hexane solutions of dithienylethenes. We assigned the red band at ca. 630 nm to fluorescence from the closed-ring form, because it appeared only for colored solid samples.

TABLE 1. Relative photochromic cyclization reaction efficiencies of dithienylethenes

Sample	Cyclization reaction efficiency 1	 2
hexane solution	1.00[a)]	1.00[a)]
colloidal solution	0.91	0.00
amorphous film	0.49	0.03

a) Taken to be unity as references. The absolute quantum yield of **2** is 0.13 [1].

TABLE 2. Relative photochromic cyclization reaction efficiencies and wavelengths at fluorescence maxima of dithienylethenes in polymer matrices.

polymer	Tg / K	1 Φ_{pc}	 λmax / nm	2 Φ_{pc}	 λmax / nm
PMMA (Ishizu)	378	1.00[a)]	472	1.00[a)]	534
PMMA (Aldrich)	368	1.03	474	0.97	532
PEMA	336	1.04	472	1.11	528
PBMA	300	1.09	469	1.41	523
PCMA	377	0.99	468	1.09	525
PS	371	0.93	470	1.10	529
PC	423	0.92	475	0.80	540
PVC	361	0.93	479	0.65	552

a) Taken to be unity as references.

The enhanced fluorescence of the closed-ring form of **1** in solid states is probably due to the efficient energy transfer from the open-ring form to the closed-ring form.

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