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Photochromic reactions of a diarylethene derivative in polymer matrices

Tsuyoshi Tsujioka [a,*], Minoru Kume [a], Masahiro Irie [b]

[a] *New Materials Research Center, Sanyo Electric Co., Ltd., 1-1 Dainichi Higashimachi, Moriguchi, Osaka 570, Japan*
[b] *Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812, Japan*

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Abstract

The sensitivity (product of molar extinction coefficient and quantum yield) of 2-(1,2-dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl)-maleic anhydride is dependent on its concentration in poly(vinyl butyral) film and on the irradiation wavelength (515 nm and 633 nm). Energy transfer from the open-ring to the closed-ring form is suggested as a possible mechanism for the time dependence of the sensitivity in the polymer film containing high chromophore concentration on irradiation with 515 nm light. © 1997 Elsevier Science S.A.

Keywords: Diarylethene; Energy transfer; Photochromism; Sensitivity

1. Introduction

Interest in the development and use of organic photochromic compounds for rewritable optical memory media has been increasing [1–18]. The indispensable properties required include the thermal stability of both isomers and high resistance to thermal and photochemical degradation. Recently, a new type of photochromic compound which has thermally irreversible and fatigue resistance properties has been developed [4,8,10,14]: diarylethenes with heterocyclic rings, such as 1,2-bis-(2-methylbenzo[b]thiophen-3-yl)-perfluorocyclopentene [14] and 2-(1,2-dimethyl-3-indolyl)-3-(2,4,5-trimethyl-3-thienyl)-maleic anhydride (**1a**).

These compounds have no thermochromicity even at 300 °C and their colored closed-ring forms are stable for more than 3 months at 80 °C [8]. Furthermore, the cycle of ring closure/ring opening can be repeated more than 10^4 times whilst still retaining the photochromic performance [8,10]. Thus diarylethene derivatives are promising photochromic compounds for rewritable optical memory media.

In general, solid state thin films containing a photochromic compound are used for photochromic memory media. When photochromic compounds are dispersed in solid polymer matrices, the reactivities are changed from those observed in homogeneous solution. For example, the thermal reverse processes no longer follow first-order kinetics [19–25]. In this study, we have investigated the photochromic reaction of **1a** in poly(vinyl butyral) and found that the sensitivity depends on both the concentration and irradiation wavelength.

2. A model of a photochromic reaction

The following equation has been used frequently to measure the photochemical quantum yield [25,26]

$$\log\left(\frac{I_{ir}/I_0-1}{I_{ir}/I_t-1}\right)=\epsilon\phi I_{ir}t \qquad (1)$$

where I_{ir} is the quantity of irradiated light, I_0 and I_t are the transmitted light intensities at times 0 and t that pass through the sample, ϵ is the molar extinction coefficient of the compound at the irradiation wavelength and ϕ is the quantum yield of the photoreaction. This equation was derived under the following conditions.

1. Light is absorbed only by the reactant molecule and not by the product molecule. The reverse photoreaction is ignored.
2. The photoreaction is of first order, i.e. a molecule reacts with a unique sensitivity by absorbing a photon.
3. Light for the photoreaction is monochromatic.
4. Light absorption by the medium and decomposition of the compounds are negligible.

We can obtain a straight line for the photoreaction by plotting the left-hand side of Eq. (1) vs. time, and derive a unique quantum yield from the slope.

In order to treat the coloration process of diarylethenes, we modified the first condition above as follows: light is absorbed

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[*] Corresponding author. E-mail: tsujioka@cosmos.yd.nm.rd.sanyo.co.jp.

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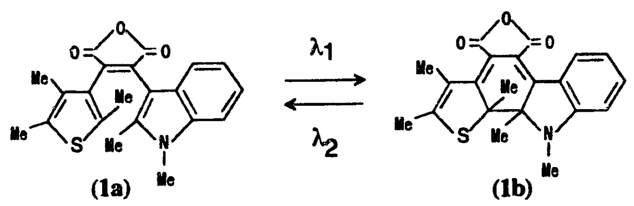

Scheme 1.

by both the reactant and product molecules; the reverse photoreaction is also taken into account.

Furthermore, for simplicity, we assumed the additional condition that the absorbance (Abs) of the sample at the irradiation wavelength is low ($\mathrm{Abs} \leq 0.2$). Under these conditions, we derived a generalized equation for the photochromic reactions.

We consider the case in which both the reactant isomer **a** (open-ring form) and the product isomer **b** (closed-ring form) absorb (molar extinction coefficients ϵ_a and ϵ_b ($\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$)) at the irradiation wavelength and react (quantum yields ϕ_a and ϕ_b). Through the photoreaction, isomers **a** and **b** can interchange (Scheme 1). The absorbance (Abs) at wavelength λ (m) is

$$\mathrm{Abs} = 1 - \exp(-2.3\mathrm{Abs}) = 1 - \exp[-2.3 \times (\epsilon_a C_a + \epsilon_b C_b)L] \simeq 2.3(\epsilon_a C_a + \epsilon_b C_b)L \qquad (2)$$

where C_a and C_b (M) are the concentrations of isomers **a** and **b** respectively and L (cm) is the sample thickness. The low absorbance approximation was used in Eq. (2). The photochromic reaction can be treated to proceed homogeneously in the approximation.

The following differential equation is derived by considering the relation between the absorbed photons and reacting molecules

$$\frac{\partial C_b}{\partial t} = -\alpha \frac{P\lambda}{S}(\epsilon_a\phi_a + \epsilon_b\phi_b)\left[C_b - \frac{\epsilon_a\phi_a}{\epsilon_a\phi_a + \epsilon_b\phi_b}C_0\right] \qquad (3)$$

where P (W) is the irradiation power, S (cm^2) is the irradiation area, C_0 is the total concentration ($C_a + C_b$) and the constant α is defined by the constants: Planck's constant $h = 6.626 \times 10^{-34}$ J s, the speed of light in a vacuum $c = 3.00 \times 10^8$ m s^{-1} and Avogadro's constant $N_A = 6.02 \times 10^{23}\ \mathrm{mol}^{-1}$ ($\alpha \equiv 2.3 \times 10^3 / hcN_A = 1.9 \times 10^4$ J m mol^{-1}). Eq. (3) is easily integrated and we obtain an equation which is directly applicable to experimental measurements

$$-\ln\left(\frac{\mathrm{Abs}(t) - \mathrm{Abs}(\infty)}{\mathrm{Abs}(0) - \mathrm{Abs}(\infty)}\right) = \alpha \frac{P\lambda}{S}(\epsilon_a\phi_a + \epsilon_b\phi_b)\delta t \qquad (4)$$

where Abs(t) indicates the absorbance in the wavelength region λ_2 at time t. It should be noted that Eq. (4) can be applied to both coloring and bleaching processes. When the photoreaction follows first-order kinetics, we obtain a linear time dependence of the left-hand side quantities, and a unique value for the total sensitivity $\epsilon_a\phi_a + \epsilon_b\phi_b$ is deduced. On the other hand, for non-first-order reactions, the plot will be curved and a unique value for the sensitivity cannot be obtained. In order to analyze such non-linear time dependence, we derived Eq. (5) from Eq. (4)

$$-\ln\left(\frac{\mathrm{Abs}(t+\delta t) - \mathrm{Abs}(\infty)}{\mathrm{Abs}(t) - \mathrm{Abs}(\infty)}\right) = \alpha \frac{P\lambda}{S}(\epsilon_a\phi_a + \epsilon_b\phi_b)\delta t \qquad (5)$$

where δt indicates the measuring time interval. The sensitivity obtained by Eq. (5) corresponds to the differential coefficient at time t of the plot with the left-hand side of Eq. (4).

3. Experimental details

We prepared three kinds of sample: benzene solution containing **1** (4.0×10^{-5} M), poly(vinyl butyral) (PVB) films containing a low concentration of **1** (0.036 M; film thickness, 12 μm) and PVB films containing a high concentration of **1** (1.0 M; film thickness, 0.4 μm). The thickness of each sample was calibrated such that the absorbances were identical and the low absorbance condition ($\mathrm{Abs} \simeq 0.2$) was satisfied at the light wavelength of the photoreaction. Usually, we can obtain the sensitivity by measuring the absorbance change in the coloring process; however, it was difficult to follow the coloring process because of the rather low conversion in the polymer film. Therefore we prepared colored film samples on glass substrates by spin coating with a cyclohexanone solution containing the colored closed-ring form of **1b** and PVB, and the absorbance change in the bleaching process was followed. No microcrystals in the samples were observed using a polarizing microscope and therefore the photochromic molecules were dispersed homogeneously in the polymer matrices.

We adopted an Ar ion laser and an HeNe laser as light sources (200 μW cm^{-2}). Light of 477 nm was used for coloring, and 515 nm and 633 nm light were used for bleaching. The absorbance of the samples was measured with a multipurpose recording spectrophotometer (Shimadzu, MPS-2000).

4. Results and discussion

Fig. 1 shows the absorption spectral changes of **1** in benzene solution. On irradiation with 477 nm light, a new peak

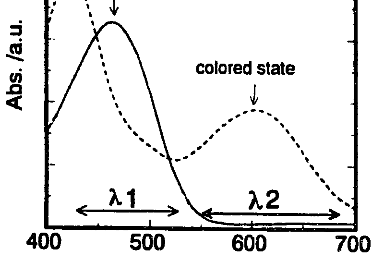

Fig. 1. Absorption spectral change of diarylethene **1** in benzene solution (4.0×10^{-5} M) on irradiation with 477 nm light.

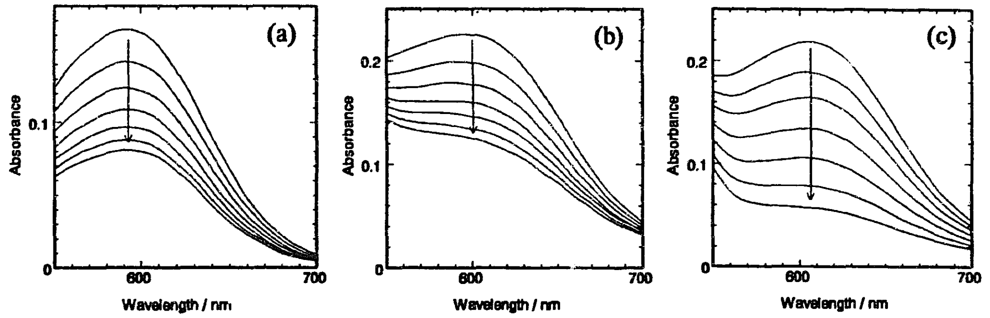

Fig. 2. Absorption spectral changes in the bleaching process on irradiation with 515 nm light. The irradiation power was 200 μW cm^{-2} and the time interval was 30 s per line. (a) Benzene solution containing **1** (4.0×10^{-5} M). (b) PVB film containing **1** (0.036 M). (c) PVB film containing **1** (1.0 M).

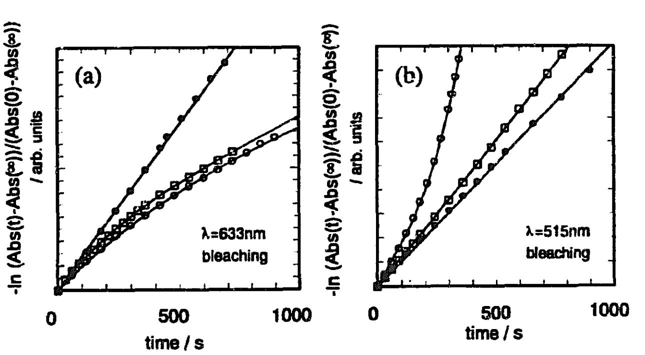

Fig. 3. Irradiation time dependence of the left-hand side of Eq. (4). Only the closed-ring form was excited with 633 nm light (a), while both isomers were excited with 515 nm light (b). ○, PVB sample (1.0 M; thickness, 0.4 μm); □, PVB sample (0.036 M; thickness, 12 μm); ●, benzene solution (4.0×10^{-5} M).

appears at 600 nm. The new peak is bleached on irradiation at 515 nm or 633 nm. The coloration/decoloration cycles can be repeated many times. Fig. 2 shows the spectral changes induced by irradiation with 515 nm light, which can excite both isomers. The absorbance of the closed-ring form in benzene solution and in the polymer film containing a low chromophore concentration decreases with irradiation time and tends to level off. On the other hand, the bleaching rate in the film containing a high concentration is much larger. This indicates that the reaction mechanism depends on the concentration of the chromophore in the polymer film.

Fig. 3 shows the irradiation time dependence of the left-hand side of Eq. (4) for the bleaching process. The time dependence for the bleaching process on irradiation with 633 nm light is also shown (note that only the closed-ring forms are excited with 633 nm light). The bleaching process in benzene solution follows first-order kinetics, while in the polymer film the bleaching process deviates from first-order kinetics. When 515 nm light is used, the bleaching process in benzene solution and in the low concentration film obeys first-order kinetics, while the plots for the high concentration sample deviate strongly from first-order kinetics. The deviation tendency is dependent on the irradiation wavelength (515 nm and 633 nm).

Fig. 4(a) and (b) show the irradiation time dependence of the sensitivity ($\epsilon_a\phi_a + \epsilon_b\phi_b$), derived using Eq. (5). When the samples are irradiated with 633 nm light, the sensitivity gradually decreases in the polymer film. In benzene solution, it remains constant. On irradiation with 515 nm light, the sensitivity of the high concentration film increases dramatically. This indicates that the ring-opening reaction sensitivity increases dramatically with time. The total sensitivity increases to as much as five times that of the initial sensitivity. In terms of the expression of the total sensitivity $\epsilon_a\phi_a + \epsilon_b\phi_b$ and the low conversion ratio, this increase indicates that the ring-opening sensitivity $\epsilon_b\phi_b$ increases. The initial quantum yield ϕ_b is 0.4, while the final quantum yield corresponds to 2.0. The only possibility for such a large increase in the quantum yield is the contribution of additional reactions through energy transfer. The photoexcited open-ring form transfers its energy to a neighboring closed-ring form, and the closed-ring molecule is transformed to the open-ring form. Fig. 5 shows schematically the reaction mechanism. When light is absorbed only by the closed-ring form, a normal ring-opening reaction occurs. On the other hand, when light

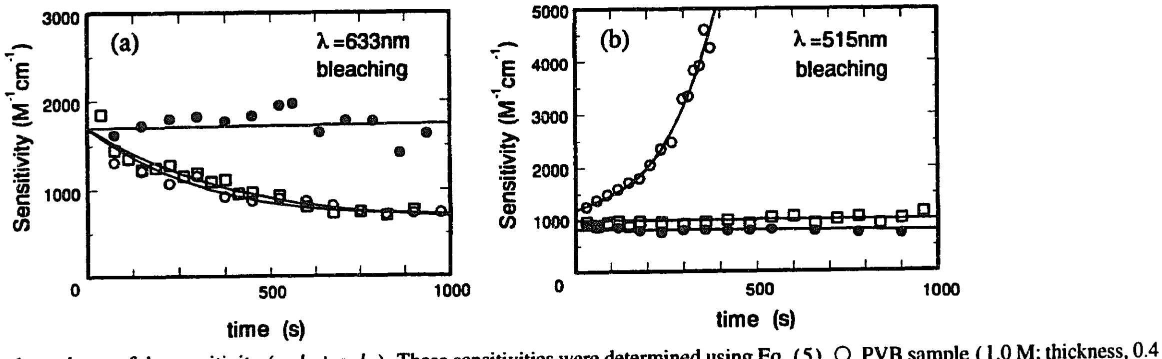

Fig. 4. Irradiation time dependence of the sensitivity ($\epsilon_a\phi_a + \epsilon_b\phi_b$). These sensitivities were determined using Eq. (5). ○, PVB sample (1.0 M; thickness, 0.4 μm); □, PVB sample (0.036 M; thickness, 12 μm); ●, benzene solution (4.0×10^{-5} M).

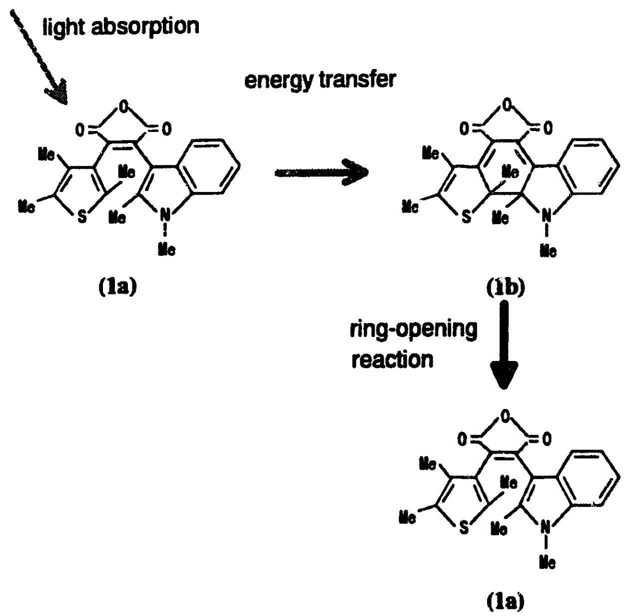

Fig. 5. Model for increasing ring-opening sensitivity with time.

is absorbed by both isomers, an additional ring-opening reaction due to energy transfer takes place when the concentration of the open-ring form is high. As a result, the ring-opening reaction sensitivity increases and the conversion ratio is suppressed.

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