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Photochromism of Clay−Diarylethene Hybrid Materials in Optically Transparent Gelatin Films

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The dispersion of clay−diarylethene hybrid materials into an ionic biopolymer, gelatin, was investigated for the successful preparation of highly functional photochromic films. A mixture of the gelatin and the clay−diarylethene hybrid material dispersed in aqueous *N*,*N*-dimethylformamide (DMF) was cast on a glass plate. The film obtained after drying at 50 °C was transparent in the visible light region and showed highly reversible coloration and decoloration by alternative irradiation with UV light of around 300 nm and visible light of around 600 nm. X-ray diffraction analysis indicated that the diarylethene molecules were able to remain in the clay interlayers without spilling into the bulk gelatin matrix. Moreover, UV−visible polarized spectroscopic analysis revealed the clay−diarylethene hybrid materials to be oriented essentially parallel to the glass plate, indicating that the diarylethene molecules are aligned as inclined interdigitated monolayers within the clay interlayers.

Introduction

The development of organic photochromic materials is strongly desired for applications in new photon-mode memory devices having fast response, high sensitivity, and a large capacity. However, because most organic photochromic compounds have the disadvantage of thermal degradation as well as poor durability after repetitive and alternative UV/visible light irradiation, the design of a practical system has yet to be realized.[1−15] Irie has successfully synthesized a diarylethene-type photochromic compound, one of the most promising materials so far.[13] However, it is important that such materials are able to exhibit a facile photochromism in solid or solid-like systems for applications in such advanced photon-mode memory devices. Here, the successful preparation of efficient photochromic solid films by the hybridization of clay minerals with dicationic diarylethene molecules has been carried out.[16,17] The diarylethene molecules were organized in hybrid films having an inclined interdigitated monolayer stacking structure, an important characteristic in such efficient and reversible photochromic behavior that can be initiated by alternative irradiation with UV light around 300 nm and visible light around 600 nm.

For the development of functional photonic materials,[18−24] the hybridization of organic compounds with layered inorganic materials such as clay minerals, polysilicates, and layered metal oxides enables the preparation of various useful functional organic compounds.[18−26] Significantly, a number of reports show that the hybridization of optically functional compounds into clay minerals have been effective in inducing photochro-

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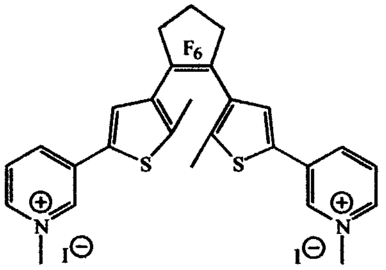
Scheme 1. Chemical Formulas for Photochromic Compound 1



mism,[2−5,16,17] nonlinear optical phenomena,[27−29] and photochemical hole burning.[30−32] These hybrid materials have usually been prepared as a powder and have thus far been shown to be inconvenient for practical applications. Clay hybrid thin films, which are nearly transparent in the visible light region, have also been prepared by the intercalation of amphiphilic azobenzenes or cationic surfactants;[28,30,31,33] however, the films were found to easily collapse by mechanical contact. Here, we report on a new methodology for the preparation of thin films of polysilicates matrixes including fine clay particles intercalated by an organic compound.[34] The present method is unique in that the hybrid materials are homogeneously dispersed in the polysilicates matrixes and, simultaneously, the hybrid clay particles are aligned on the quartz glass by a spin-coating technique. It is essential that the matrix material for the film be highly transparent for its application to photofunctional devices.

The present work describes the synthesis, structural analysis, and photochromic characterizations of a highly transparent hybrid film, which uses gelatin as a matrix capable of homogeneously dispersing and uniformly organizing the clay−diarylethene hybrid materials.

Experimental Procedures

The Intercalation of 1,2-Bis(2′-methyl-5′-(1″-methyl-3″-pyridinio)thiophen-3′-yl)-3,3,4,4,5,5-hexafluorocyclopentene Diiodide (1) in Montmorillonite Clays. Clay−diarylethene hybrid materials were synthesized by ion exchange with diarylethene cations (**1**: cf. Scheme 1) in an aqueous clay suspension. Purified standard sodium montmorillonite clay, $Na^{0.33+}[(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2 \cdot nH_2O]^{0.33-}$, with a cation-exchange capacity (CEC) of 1.19 mequiv/g obtained from the Clay Science Society of Japan was used without further purifications (the particle size, <2 μm). The cationic diarylethene (**1**) was synthesized in accordance with previous reports.[16,17]

One gram of the montmorillonite powder was dispersed in 500 mL of distilled and deionized water by sonication. An equivalent amount (476 mg) of the iodide salts of **1** was added in powder form to the montmorillonite suspension under magnetic stirring at room temperature. The resulting suspended mixture was kept heated one more night at 60 °C to complete the intercalation of **1** within the montmorillonite interlayers, although the resulting filtrate solution does not include any significant amount of **1**. A light-brown precipitate was isolated by a membrane filter (pore size, 0.20 μm) and dried overnight in vacuo at room temperature to yield a dry clay−**1** hybrid material in solid form. This was then ground in an agate mortar and used as prepared for the experiments.

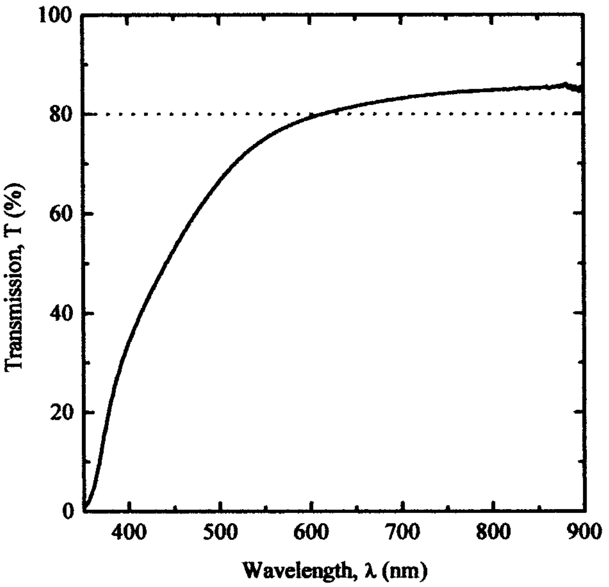


Figure 1. Transmission spectra of the gelatin film involving the clay−**1** hybrid materials.

Preparation of the Clay−1 Hybrid Films in the Gelatin Matrixes. One gram of the pure grade gelatin purchased from Wako Chemical Industries, Ltd., was dissolved in 9 mL of the distilled and deionized water at 50 °C. A mother solution of the clay−**1** in *N*,*N*-dimethylformamide (DMF) was prepared by the dispersion of 100 mg of the hybrid powder in 4 mL of DMF by sonication. A control experiment showed that the diarylethene was not released from the hybrid powder upon dispersion into the DMF. One milliliter of this mother solution was added to 9 mL of an aqueous gelatin solution (ca. 0.11 g/mL) at 50 °C under magnetic stirring for several additional hours. One milliliter of the mixed suspension was then cast on a glass plate using a pipet and dried at 50 °C for 3 days to give a transparent film with a thickness of about 150 μm. The obtained film is, hereafter, referred to as the "hybrid gelatin film."

Characterizations. X-ray diffraction analysis of the photochromic film samples was carried out with a RINT 2000 diffractometer (Rigaku) using a Cu $K\alpha$ radiation source operating at 40 kV and 40 mA as the applied voltage and current, respectively. The absorption spectra were recorded in the region of 350−900 nm on a JASCO V-550 spectrophotometer. The UV−visible polarized absorption spectra were also recorded on this spectrophotometer with a JASCO polarizer unit attachment (Model RSH-452). The photochromic changes were monitored by irradiation with UV and visible light obtained from a 300-W medium-pressure mercury arc lamp (Eikosha Corp., Model PIH300) through UTVAF-50S-34U and SCF-50S-52Y cutoff filters from SIGMA KOKI Co., Ltd., respectively.

Results and Discussion

Photochromism of the Hybrid Gelatin Film. Figure 1 shows a high transparency in the wavelengths of visible light regions, particularly at 600−900 nm in clay−**1** hybrid gelatin films having a thickness of ca. 150 μm. The high transparency is thought to be attributed not only to the similar refractive indexes (ca.

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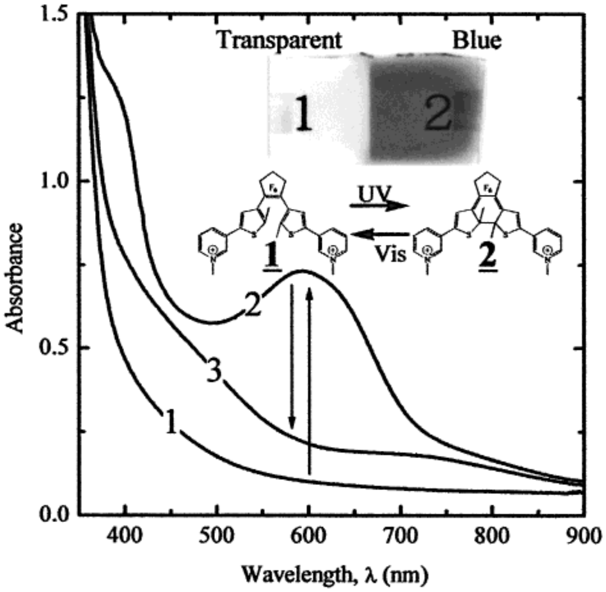

Figure 2. Absorption spectra of the present transparent film: (1) before light irradiation; (2) after UV irradiation; and (3) after visible light irradiation (2). The insertion shows the transparent film irradiated by <300 nm. The left-half area of the film was not exposed to the light using black screen paper.

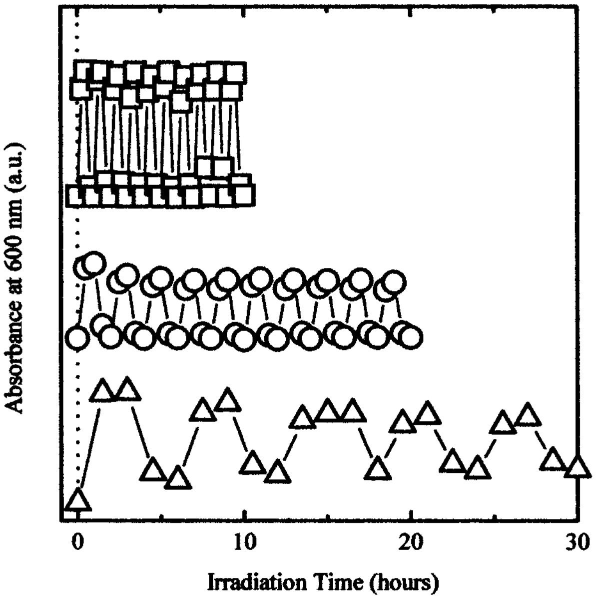

Figure 3. Changes in the absorbance at 600 nm with alternative irradiation of UV and visible light. Diarylethene, **1**, in methanol (□); as a powder sample of the clay−**1** hybrid placed on a SiO_2 slide (○); and the present gelatin−clay−**1** hybrid film on a SiO_2 slide (△).

1.5) of the gelatin and the clay layers but also to the fact that the gelatin network possesses zwitterionic terminals, which interact electrostatically with the anionic clay surface in aqueous suspensions.

UV light irradiation of the clay−**1** hybrid film below 300 nm resulted in a change from colorless to blue. However, the resulting blue color faded with visible light irradiation at around 600 nm. The interconversion between the colorless **1** and the colored **2** may be explained by the equation in Figure 2. A photograph of the hybrid gelatin film is shown as an insertion in Figure 2, depicting about half the area of the film, which was exposed to UV light. The hybrid gelatin films showing such changes in color retained high homogeneity and clearness.

In the spectral change of the hybrid gelatin film (Figure 2), the absorption maxima due to the blue photoproduct **2** appeared at around 400 and 600 nm with UV light irradiation below 300 nm, while the absorption maxima of **2** decreased by visible light irradiation above 500 nm, though the reversal process was rather slow. This can be explained by the efficiency of the reversal process, which is approximately one-tenth that of the forward process due to the long π-conjugation of compound **1**.[35,36]

The spectral interconversion between **1** and **2** was monitored at 600 nm, as shown in Figure 3, by alternative irradiation with UV and visible light in methanol (□), and as a powder sample of the clay−**1** hybrid on a SiO_2 slide (○), or the present film sample of the gelatin−clay−**1** hybrid on a SiO_2 slide (△). Diarylethene, **1**, dissolved in methanol retained high reversibility, even with repeated alternative irradiation, as reported by Irie and co-workers.[13,36,37] Though the interconverted clay−**1** hybrid powder and the hybrid gelatin film show reversibility during repeated irradiation by UV and visible light, the amount of the colored **2** produced by UV light irradiation slightly decreases by repetitive alternative irradiation (Figure 3). Interestingly, the diarylethene-type molecules were found to exist as a mixture of the parallel and antiparallel isomers[36] and were photochemically interconvertible only in the case of the antiparallel isomers. Because **1** can exist as an equal mixture of the two isomers before the irradiation procedures, the quantum yield of the formation of **2** did not exceed 0.5. Hence, the low photochromic reversibility is assumed to be due to the entrapment of the photoinactive form of **1** (parallel form) on the anionic sites of the clay surface (ca. 0.9 nm) because there is good agreement between the distance of the anionic sites and that of the cationic nitrogen atoms of the photoinactive parallel **1** (ca. 1.0 nm).[16,17]

Table 1. Estimation of the d_{001} Values for Montmorillonite Clay, the Powder Clay−1 Hybrid, and Clay−1 Hybrid Materials Dispersed in the Gelatin Polymer Matrix

samples	d_{001} (nm) powder	d_{001} (nm) gelatin matrix
montmorillonite clay	1.23	1.21
montmorillonite clay−**1** hybrids	1.80	2.17

X-ray Diffraction of the Hybrid Gelatin Film. Table 1 shows the d_{001} values of the montmorillonite clay powder, the powder clay−**1** hybrid materials, and the clay−**1** hybrid gelatin film. The d_{001} value of the clay−**1** hybrid materials was larger than that for montmorillonite clay, indicating that the photochromic compound, **1**, was intercalated in the clay and contributed to the opening of the interlayer spaces. The d_{001} values of montmorillonite clay without **1** are little affected both for the clay powder and in the gelatin matrixes. In contrast, the layer distances become much larger when the clay−**1** hybrid is dispersed in the

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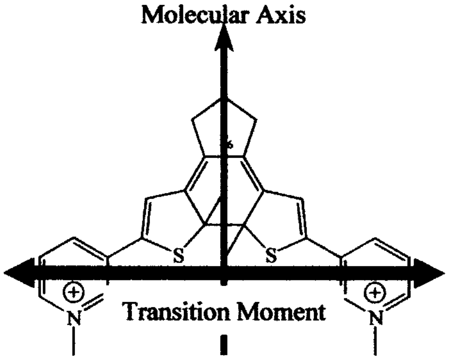
Scheme 2. Relationship between the Molecular Axis and Optical Transition Moment at 600 nm in the Closed-Ring 1 Molecules



gelatin matrix and not used as a powder. The difference is attributed to the invasion of the DMF solvent molecules into the clay interlayers together with **1**. XRD analysis indicates that compound **1** remains adsorbed in the clay interlayers, even when dispersed in the gelatin matrixes; that is, no photochromic **1** is present outside of the clay layers or in the gelatin matrix during the film-preparation process.

UV−Visible Polarized Spectroscopy of the Hybrid Gelatin Film. The alignment of photochromic **1** is considered to tilt from 40° to 69° toward the gelatin matrix film, judging from the gallery height (d_{001} − 0.96 nm layer thickness) and the molecular length of **1** (L = 1.3 nm). Here, electronic transition absorption spectroscopy with polarized UV−visible light was useful in evaluating angle γ of the molecular axis from the normal line on the silica glass slide.[34,39,40] This is based on the assumption that the guest molecules with some chromophores are aligned in a regular manner within the film. Here, angle γ can be expressed by the following equation:

$$\begin{aligned} R &= A_y/A_x \\ &= \{2[\sin^2\theta + \sin^2\alpha(3\cos^2\theta - 1)] - \\ &\qquad (3\sin^2\alpha - 1)(3\cos^2\theta - 1)\sin^2\gamma\}/ \\ &\qquad\qquad \{2\sin^2\theta + (2 - 3\sin^2\theta)\sin^2\gamma\} \quad (1) \end{aligned}$$

R is the dichroic ratio of A_y to A_x, representing the absorption intensities for the horizontal and the vertical polarized incident lights, respectively. θ and α indicate the angles of the molecular axis to the optical transition moment and of the incident light against the substrate plane, respectively. The film has an optical anisotropy due to the regular arrangement of the guest molecules in the hybrid film because the R value varies according to α. Accordingly, the tilt angle γ of **1** was obtained by using eq 1, assuming that $\theta = 90°$ at 600 nm (cf. Scheme 2), and judging from the transition moment previously reported.[41,42]

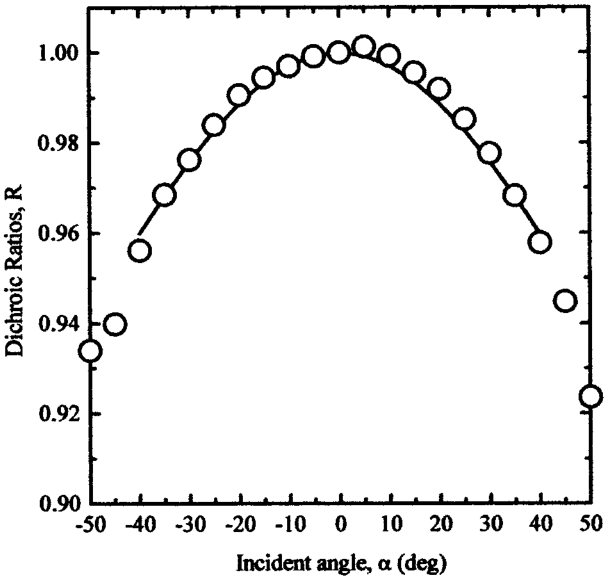


Figure 4. Incident angle (α) dependence of the dichroic ratios (R) of the clay−**1** hybrid materials in the present transparent gelatin film. Symbols denote experimental data with the solid line determined in accordance with eq 1.

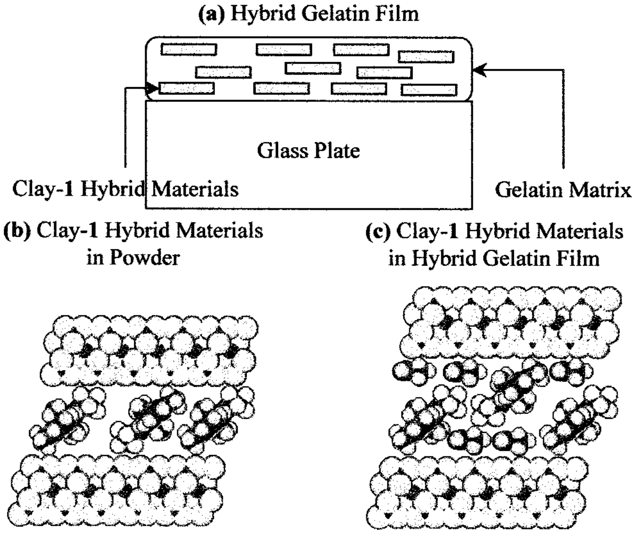


Figure 5. Possible oriented models: (a) clay−**1** hybrid materials in the optically transparent film; (b) intercalated **1** molecules in clay powder samples; and (c) intercalated **1** molecules in clay dispersed in the optically transparent film.

Figure 4 shows the experimental correlation between R and α in the hybrid gelatin film. The R value of the hybrid sample was dependent on the α values, with a maximum at α = 0°, which indicates that the intercalated **1** molecules are oriented not only in the clay interlayers but also on the glass plate. The clay−**1** hybrid materials are concluded to be parallel in this hybrid gelatin film on the glass plate (Figure 5a) on the assumption that the clay particles have a disklike shape.[43] Angle γ was estimated to be ca. 52.1° by applying eq 1 to the correlation between R and α, and at the same time, d_{001} was determined to be 1.76 nm using the equation $d_{001} = L \times \sin(90° - \gamma)$. The obtained d_{001} was determined to be 1.80 nm in the case of the

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powder clay−**1** hybrid materials (Figure 5b). The difference of 0.37 nm between the d_{001} values of the hybrid gelatin film and the powder clay−**1** suggests that DMF is incorporated as a monolayer together with the guest **1** layer in the clay−**1** hybrid materials, on the point that the DMF molecules possess a similar size (ca. 0.4 nm) in the interlayers as can be seen in Figure 5c.

Conclusions

The present paper describes the successful hybridization of a gelatin matrix for the synthesis of transparent films with the capacity for characteristic photochromism by the dispersion of the montmorillonite−diarylethene hybrid materials as a matrix in a gelatin polymer. Upon irradiation with UV/visible light, the intercalated diarylethene molecules undergo a photochemical interconversion between a colorless **1** and blue-colored **2** with high reversibility. Moreover, the guests molecules can safely and stably be sustained in the clay interlayers without spilling into the gelatin bulk. X-ray diffraction analysis of the dispersed film involving the montmorillonite−**1** hybrid showed that the diarylethene guest **1** is anistropically accommodated with DMF in the film on the glass plate. These films show great potential in the use of the application of clay minerals for advanced optical materials.

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