

Photochromic Behavior and Its Stability of a New Bifunctional Dye Composed of Spirobenzopyran and a Cinnamoyl Moiety

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Abstract: A novel bifunctional dye composed of spirobenzopyran and a cinnamoyl moiety was prepared and its photochromic behavior under the illumination of monochromatic UV light was investigated. This colorless bifunctional dye exhibits typical photochromism in both the film and in solution, through the structural and geometrical transformation from spirobenzopyran to merocyanine accompanied by a photocrosslinking reaction between the cinnamoyl moieties. Two kinds of photochemical reaction were selectively achieved by irradiation with monochromatic UV light at wavelengths of 275 and 365 nm, respectively. The effect of the selective photochemical reaction on the photochromism of the dye and its decaying behavior was investigated.

Keywords: spirobenzopyran, cinnamoyl moiety, photochromism, selective photochemical reaction.

Introduction

Organic photochromic compounds have been investigated for its potential use in reversible information memory media.¹⁻⁴ Light and thermal treatment will control their reversible photochromic properties at an ambient condition. Spirobenzopyran is probably the most well-known class of organic photochromes to generate colored merocyanines under illumination of UV light.^{5,6} However, the merocyanine structure is thermally unstable inherently to revert to the spirobenzopyran structure. It is clear that the stability of the colored form of spirobenzopyran should be improved essentially for its practical application, preventing from erasing the recorded information.⁷

Besides photochromism, photocrosslinking reaction is another well known photochemical reaction employed for industrial purpose frequently. Particularly, polymers containing unsaturated aromatic acid or ester units, for example the cinnamic acid or cinnamic ester derivatives are used for studying the phototransformation phenomena that occurs under illumination of UV light. The photosensitivity of these materials is mainly attributed to the π -electron density of the photoactive chromophore (i.e. -CH=CH-Ar).

Among many promising photosensitive groups, the cinnamoyl derivatives have been well employed for the synthesis of photocrosslinkable polymers due to its high sensitivity to UV radiation ($\lambda=250-280$ nm) and high photocrosslinking efficiency.⁸⁻¹¹

The effect of photocrosslinked chalcone or cinnamoyl moieties on the stability of photochromism was investigated intensively.^{12,13} In our recent study, we used the photosensitive polymer containing unsaturated aromatic ketone of chalcone to improve the stability of photochromism after UV irradiation. In that experiment, we irradiated the UV light whose wavelength is ranging from 290-390 nm that is broad-banded. Therefore, photochromism and photocrosslinking between chalcone moieties occurred concomitantly. Then, the photochromic behavior was relatively retarded due to photocrosslink between chalcone groups in the repeating unit. On the while, the stability of photochromism was improved resulting from the geometrical hindrance for Z/E transformation and ring closure.

In this paper, we designed and synthesized a new photochemically bifunctional dye containing a cinnamoyl moiety as a photocrosslinkable group and photochromic spirobenzopyran. In order to investigate the photochromic property of a new dye, we also employed the conventional spirobenzopyran monofunctional dye. In the experiment to observe the photochromism, we used the monochromatic UV light

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rather than the broadband UV light. When the new bifunctional compound is illuminated with two different monochromatic UV wavelengths of 365 and 275 nm sequentially, photochromism and photocrosslinking reaction will occur almost selectively. The stability of photochromism was also investigated to observe the dynamic behavior of the diffraction efficiency. We can expect higher stability of photochromism of the bifunctional dye than that of the spirobenzopyran dye itself when it was doped into polymers such as poly(methyl methacrylate) (PMMA) and photosensitive poly(vinyl cinnamate).

Experimental

General. All reagents were purchased from Aldrich Chem Co. and used without further purification unless otherwise mentioned. *N,N*-dimethylformamide (DMF), ethyl acetate, and chloroform were purified by standard distillation methods for using as solvents. ¹H-NMR spectra were obtained in CDCl₃ with a Varian INOVA-400 spectrometer.

Infrared spectra were recorded on Bruker IFS66v FT-IR spectrometer under dry air purge. Thin film of the sample of compound 2 doped polyvinylcinnamate (PVCi) was cast on KBr window were prepared from tetrahydrofuran solution. After the solvent was evaporated, the films were stored under vacuum at 50 °C for at least 3 hrs to remove residual solvent completely. The film on the KBr window was subjected to UV irradiation for a designated time ($\lambda=275$ nm, $I=0.48$ mW/cm², $t=15$ min) and the spectra were taken before and after UV exposure.

UV-Vis Absorption Spectral Analysis of the Photochromic Materials. UV-Visible absorption spectroscopic study was performed with a Hewlett Packard 8453 spectrophotometer (PDA type, $\lambda=190$ -1100 nm). For inducing photochromism or photocrosslinking reaction, a Thermo Oriel 4269 Xe lamp (1 kW) equipped with Thermo Oriel 74000 monochromator was used to set the excitation wavelength. Intensities of the monochromatic UV light on the film surface were 1.44 and 0.48 mW/cm² as the wavelengths are set at 365 and 275 nm respectively, which were measured with a broadband power/energy meter model 13PEM001 (Melles Griot).

Photochromic Holographic Experiment: Measurement of the Diffraction Efficiency. We made experimental setup for recording the gratings and measuring the first-order diffracted light intensity. Argon ion laser ($\lambda=514$ nm, $I=22$ mW/cm²) was used for fabricating the diffraction grating and a diode laser ($\lambda=830$ nm) was used to probe the recorded gratings. The beam was expanded using a microscope objective and a spatial filter. The pump beams were passed through a spatial filter arrangement to obtain planar collimated light. Two vertically plane polarized (s- & s-) light beams with equal intensity were obtained by adjusting the half wave plate and the three polarizers appropriately, gen-

erating the holographic grating. The angle between the interfering two beams is set to be 28°. Time-resolved variation of the first order diffraction was monitored online with a probe beam from a diode laser (p-polarized $I=0.2$ mW/cm²). Standard lock-in detection techniques were used to maximize the signal-to-noise ratio (Lockin-amplifier, EG & G 7260 DSP; Optical chopper, SR540, 4 Hz-3.7 kHz).

The probe beam was diffracted by the gratings with an efficiency η that is defined as the ratio of the intensities of the diffracted to the incident beam ($\eta = I_{diff}/I_0$).

Synthesis of *N*-ethoxyl-3',3'-dimethylspiro(2*H*-5-nitro-1-benzopyran-2,2'-indoline) (Compound 1). A solution of 2,3,3-trimethyl-3*H*-indole (6.0 g, 38 mmole) and 2-bromoethanol (7.4 g, 46 mmole) in ether (100 mL) was refluxed with stirring for 4 hrs. Then, the reaction mixture was stirred for one hour at room temperature and the precipitated solid (8.2 g) was collected by filtration. After the crude solid being washed with acetone, a portion of the solid (1.82 g, 5.5 mmol) was dissolved in NaOH aqueous solution (2 M, 8 mL). The resultant *N*-ethoxyl-substituted indoline was extracted with chloroform. The organic layer was dried with anhydrous Na₂SO₄ and the solvent was evaporated. The residue and 2-hydroxy-5-nitrobenzaldehyde (0.874 g, 5.2 mmole) were dissolved into 50 mL DMF again. The mixture was stirred at 60 °C for 4 hrs and poured into 200 mL of distilled water. After the resultant solid being collected and recrystallized from acetone, a red-brown crystal (1.92 g) was obtained with yield 75%. m.p. 163 °C.

¹H-NMR (400 MHz, CDCl₃): δ (ppm) 8.00 (d, J=7.5Hz, 1H), 7.99 (s, 1H), 7.18 (t, J=7.5Hz, 1H), 7.10 (d, J=7.2Hz, 1H), 6.88~6.94 (m, 2H), 6.77 (d, J=7.8Hz, 1H), 6.68 (d, J=7.2Hz, 1H), 5.89 (d, J=7.2Hz, 1H), 3.80~3.85 (m, 1H), 3.71~3.76 (m, 1H), 3.42~3.49 (m, 1H), 3.30~3.36 (m, 1H), 1.28 (s, 3H), 1.17 (s, 3H)

EA (CHN) analysis calcd for C₂₀H₂₀N₂O₄ (MW: 352.38): C, 68.17; H, 5.72; N, 7.95. Found; C, 68.78; H, 6.80; N, 7.97.

Synthesis of *N*-ethoxy cinnamate-3',3'-dimethylspiro(2*H*-5-nitro-1-benzopyran-2,2'-indoline) (Compound 2). Compound 1 (1.85 g, 0.5 mmole) and triethylamine (2.02 g, 2.0 mmol) were dissolved in THF (50 mL) and cooled in an ice bath. THF (5 mL) solution of cinnamoyl chloride (1.63 g, 1 mmole) was added dropwise into the mixture under vigorous stirring. Then the mixture was stirred for 6 hrs at room temperature and the reaction was completed. The mixture was poured into water and extracted with CHCl₃. The organic layer was washed with water repeatedly until it becomes neutral and was dried under Na₂SO₄. The crude product was purified by column chromatography on silica gel (6:1=chloroform/hexane) and 1.63 g of light-yellow solid was obtained with yield 65%. m.p.136 °C.

¹H-NMR (400MHz,CDCl₃): δ (ppm) 8.00 (d, J=7.5Hz, 1H), 7.99 (s, 1H), 7.64 (d, J=15.9Hz, 1H), 7.36~7.50 (m, 5H), 7.23 (t, J=7.5, 1H), 7.10 (d, J=7.2Hz, 1H), 6.88~6.93

(m, 2H), 6.76 (d, $J=8.4\text{Hz}$, 1H), 6.73 (d, $J=7.2\text{Hz}$, 1H), 6.30 (d, $J=15.9\text{Hz}$, 1H), 5.89 (d, $J=10.2\text{Hz}$, 1H), 4.35 (t, 2H), 3.54~3.64 (m, 1H), 3.46~3.54 (m, 1H), 1.28 (s, 3H), 1.17 (s, 3H)

EA (CHN) analysis calcd for $\text{C}_{29}\text{H}_{26}\text{N}_2\text{O}_5$ (MW 482.53): C, 72.18; H, 5.43; N, 5.81. Found; C, 72.56; H, 6.83; N, 5.98.

Results and Discussion

Synthesis and Characterization. Photochemically bifunctional dye (compound 2) containing photochromic spirobenzopyran and a cinnamoyl moiety was synthesized successfully as illustrated in Figure 1. *N*-Ethoxyl-3',3'-dimethylspiro-(2*H*-5-nitro-1-benzopyran-2,2'-indoline) (compound 1) was prepared by reacting *N*-ethoxyl-2,3,3-trimethyl-3*H*-indole with 2-hydroxy-5-nitro-benzaldehyde in DMF. Then cinnamoyl chloride was attached to compound 1 by esterification to produce compound 2 in 65% yield.

The structure of each compound was confirmed by proton NMR spectroscopic analysis. The chemical shifts of the ethylenic protons (-CH=CH-) in compound 2 were observed at 6.30 (1H, d, $J=15.9\text{ Hz}$) and 7.64 (1H, d, $J=15.9\text{ Hz}$) which indicate *trans*-conformation. These analyses proved that the compound was successfully synthesized by our designed procedure.

Absorption Spectral Analysis of a Bifunctional Photochromic Dye in the Solution State. Figure 2 shows the absorption spectra of compound 1 and 2 in chloroform after irradiating monochromatic UV light at 365 nm. The spectra of two compounds before irradiation were also shown as an

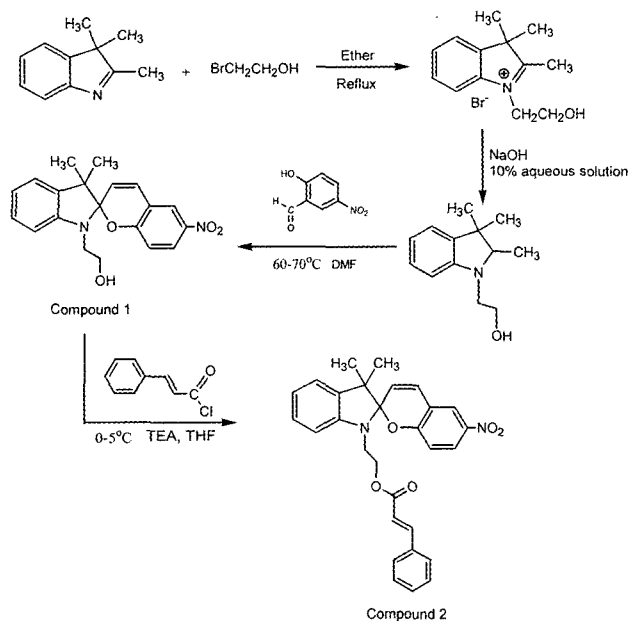


Figure 1. Synthetic procedure for the bifunctional dye composed of a cinnamoyl moiety and photochromic spirobenzopyran.

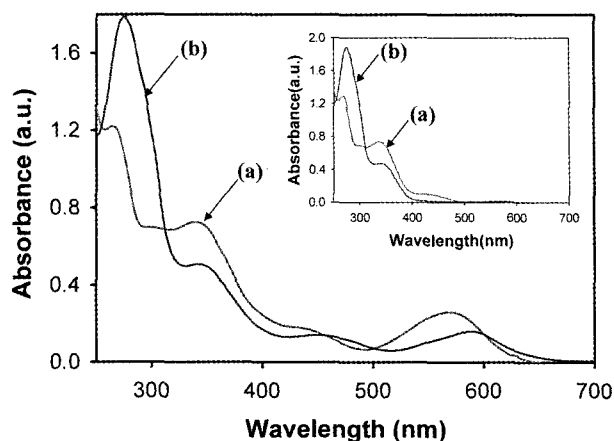


Figure 2. Absorption spectra of compound 1 (a) and compound 2 (b) in chloroform after irradiation of monochromatic UV light ($\lambda=365\text{ nm}$) at room temperature. *Inset: the spectra before irradiation.

inset of Figure 2. It was observed clearly that the characteristic absorption band appears around 576 nm in compound 1 and 585 nm in compound 2 after irradiation of monochromatic UV light ($\lambda=365\text{ nm}$), respectively. Bifunctional dye exhibits different absorptions from spirobenzopyran with two characteristic absorption bands at 278 and 585 nm after 365 nm UV irradiation. The former absorption band is due to $\pi-\pi^*$ transition of the double bond in the cinnamoyl moiety of bifunctional dye and the latter band is due to the transition of the lowest bandgap in merocyanine form of spirobenzopyran indeed. Due to the dilution effect from cinnamoyl groups, no aggregation of the spirobenzopyran moieties was observed.

Figure 3 shows the absorption spectra of compound 2 in chloroform with irradiation of monochromatic UV light at 365 nm (a) and 275 nm (b), respectively. Compound 2 shows photochromism in chloroform mainly under irradiation of 365 nm light although small decrement at 275 nm was observed owing to formation of a small extent of photodimer (Figure 3(a)). When we illuminate 275 nm UV light on the sample, only significant decrease of the absorbance at 275 nm can be observed without any formation of merocyanine (Figure 3(b)). In a dilute solution of the dye, photochromism and photocrosslinking reaction can be driven selectively under irradiation at different wavelength of UV light.

The colored species of compound 2 shows the absorption maximum at 585 nm after irradiation at 365 nm, which implies *trans*-conformation of merocyanine chromophore. If the wavelength of UV light is switched from 365 to 275 nm (switching time < 2 sec), the absorption of the cinnamoyl moiety decreases distinctly at 275 nm followed by saturation of the absorbance at 585 nm. This fact means that the cleavage of double bond occurs in the cinnamoyl group

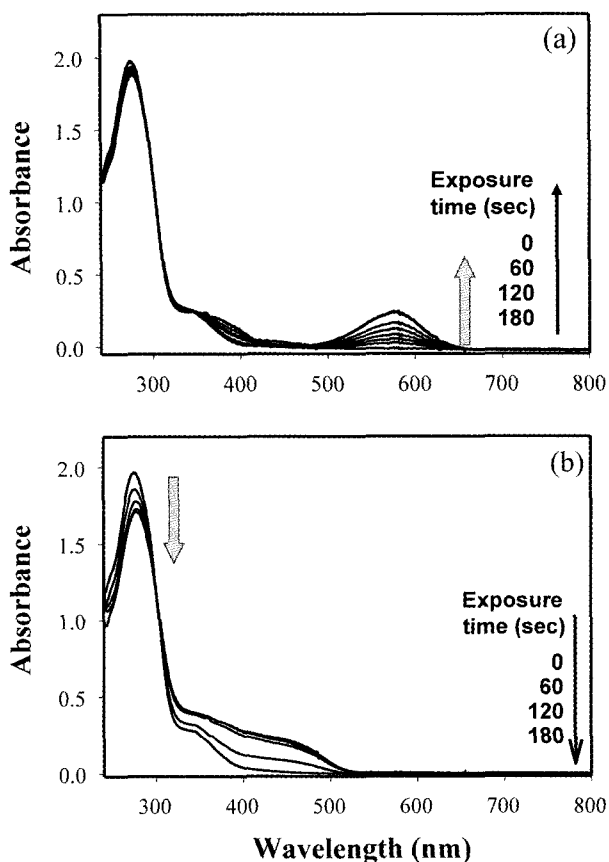


Figure 3. Absorption spectra of compound 2 in chloroform (5.515×10^{-5} mol/L) during irradiation of different monochromatic UV light at room temperature. *Wavelength of the illuminated light (a) 365 nm and (b) 275 nm.

during UV irradiation at 275 nm. Compound 2 bearing the photochromic spirobenzopyran and cinnamoyl moiety can have two major different photoproducts under irradiation at 275 and 365 nm, which is attributed to the selective photochemical reaction (See Figure 4).

Absorption Spectral Analysis of the Film Sample Doped with Bifunctional Dye. Poly(vinyl cinnamate) (PVCi) is used widely as one of photosensitive polymers.^{14,15} Figure 5 shows the absorption spectral change of PVCi film doped with compound 2 (7 wt%) during illumination of monochromatic UV light at 275 nm (a) and 365 nm (b), respectively. In the film state, PVCi doped with compound 2 exhibits the fast decrease of absorbance around 275 nm under illumination of 275 nm UV light. Photocycloaddition in cinnamoyl groups induced the maximum degree of photocrosslink when the UV irradiation time reaches 300 sec ($I=0.48$ mW/cm²). Since increment of the absorbance at 580 nm is almost negligible, spirobenzopyran in host polymer is almost inert photochemically at this wavelength. Therefore, as same as the solution state, photodimerization is predominant at this wavelength irradiation. When we change the wavelength of

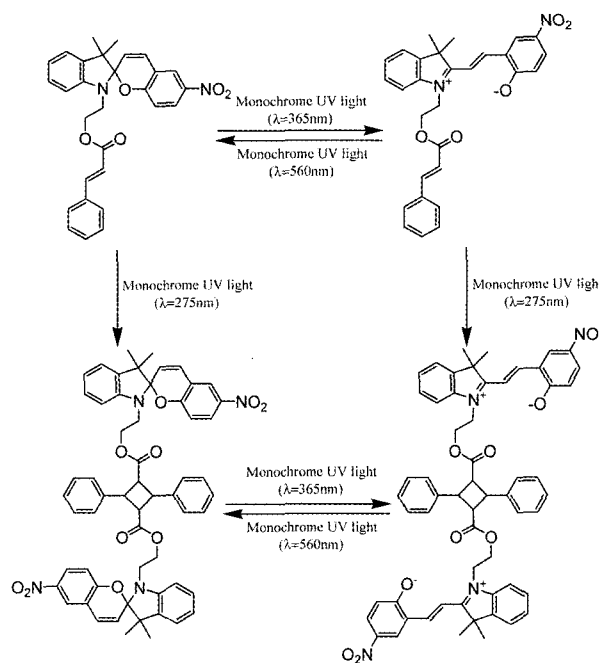


Figure 4. The photoproducts from expected photochromism and photocrosslinking reaction of the bifunctional dye during irradiation at different monochromatic UV lights (275 nm/365 nm/560 nm).

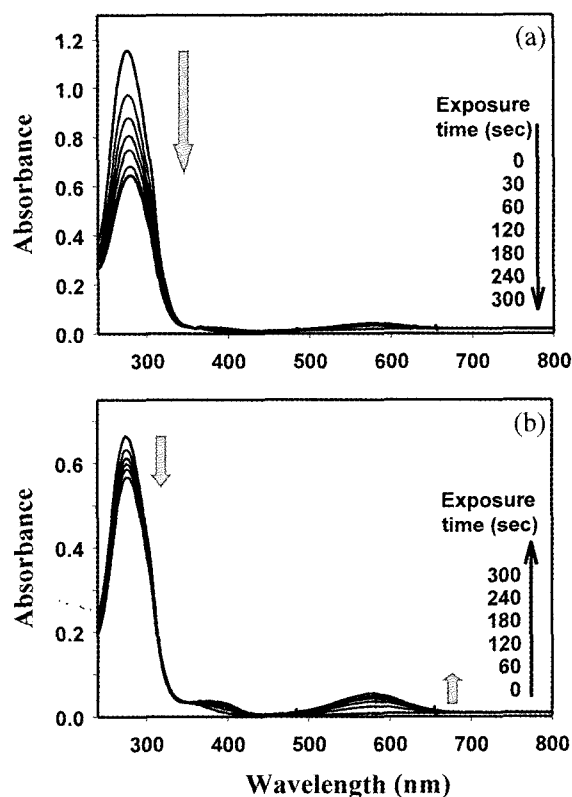


Figure 5. Absorption spectral change of poly(vinyl cinnamate) doped with compound 2 under irradiation of monochromatic UV lights. (a) 275 nm UV irradiation and (b) 365 nm UV irradiation.

monochromatic UV light from 275 to 365 nm shortly, the colored transformation of bifunctional dye exhibits the increment of the absorption at 580 nm. In Figure 5(b), we could also observe small decrement of the absorbance at 275 nm, which is attributed to small extent of photocycloaddition resulting from relatively higher concentration of the dye in the film and photoreaction under weak probe beam illumination of 275 nm repeatedly.

Figure 6 shows the comparison of the FT-IR spectra of compound 2 doped PVCi film obtained before and after UV irradiation ($\lambda=275$ nm, $I=0.48$ mW/cm², $t=15$ min). The significant changes in the IR spectrum of the sample III that occur after exposure to UV light are illustrated in Figure 6. The -C=C- stretching mode at 1637 cm⁻¹ and the unsaturated ester carbonyl band at 1711 cm⁻¹ are both observed to decrease significantly with the UV exposure time. Concurrently, a new band, attributed to a saturated ester carbonyl stretching band appeared at 1738 cm⁻¹. The observation clearly explains the photocrosslinking reaction depicted in Figure 4.

Compound 1 doped PMMA (sample I), compound 2 doped PMMA (sample II), and compound 2 doped PVCi (sample III) are employed to study the effect of photocycloaddition between cinnamoyl moieties on decaying behavior of photochromism. In order to compare the decaying behaviors of photochromism, we firstly irradiated 365 nm UV light for 300 sec and switched to irradiate 275 nm UV light for 900 sec in the sample III and the sample II. The sample I was only illuminated by 365 nm UV light for 300 sec. The kinetic evaluation was carried out by measuring absorption change during the thermal decolorization in the film state shown in Figure 7. The rate of decolorization was measured with decrease of the absorbance at λ_{max} and the decaying curve was well fitted to the single exponential decay function (1).^{16,17}

$$\ln[A(t) - A(\infty)/A(0) - A(\infty)] = -k t \quad (1)$$

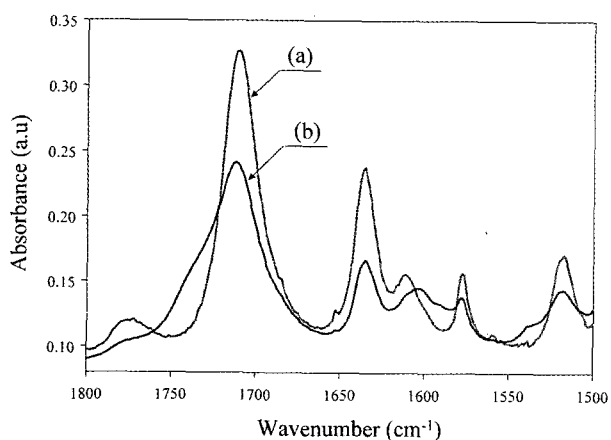


Figure 6. The comparison of the FT-IR spectra of poly(vinyl cinnamate) film doped with compound 2 (sample III) obtained before and after UV irradiation.

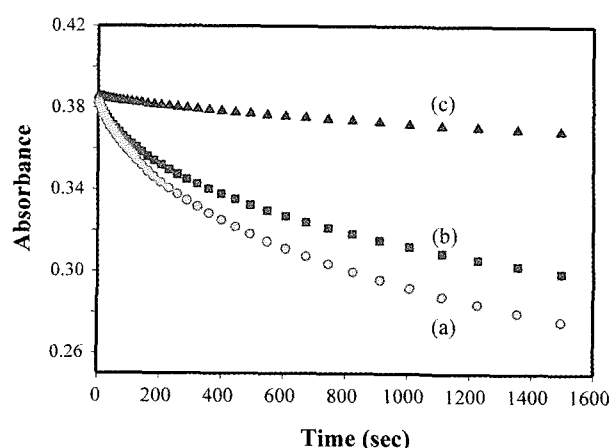


Figure 7. The absorbance change during decolorization process during the irradiation of 560 nm monochromatic UV light (a): sample I, (b) sample II, and (c) sample III.

where $A(\infty)$ is the residual absorbance after long term exposure and k is the rate constant. In the decolorization process (see Figure 7), the rates are listed in Table I that shows the rate (k) of the sample III is much smaller than that in PMMA (sample II). It is also observed that sample II displays a lower rate (k) than sample I as compound 1 doped PMMA in film state. It means that during the irradiation of monochromatic UV light at 275 nm, photocycloaddition between the cinnamoyl moieties in PVCi and compound 2 would limit the *Z/E* transformation and ring closure from *trans*-merocyanine dye into spirobenzopyran. It would be saying that the decolorization of compound 2 after UV irradiation is much retarded ($k=0.00096$ sec⁻¹) by increasing steric hindrances resulting from intramolecular and intermolecular photocycloaddition of cinnamoyl moieties.

We investigated the effect of the UV irradiation time on the decaying behavior of the PVCi doped with compound 2 precisely. It is clear that the stability of the merocyanine form of compound 2 is improved with the irradiation time at 275 nm followed by irradiation of monochromatic UV light at 365 nm for 5 min (See Figure 8). 5 min irradiation at 365 nm is the optimum light dose of light irradiation to reach the saturated absorbance at 580 nm. Table II is listed the calculated parameters of the thermal decolorization

Table I. Calculated Parameters from the Decaying Behavior of the Absorbance at 560 nm. *sample I: PMMA doped with compound 1, sample II: PMMA doped with compound 2, sample III: PVCi doped with compound 2

Sample	k (sec ⁻¹)
sample I	0.00367
sample II	0.00179
sample III	0.00096

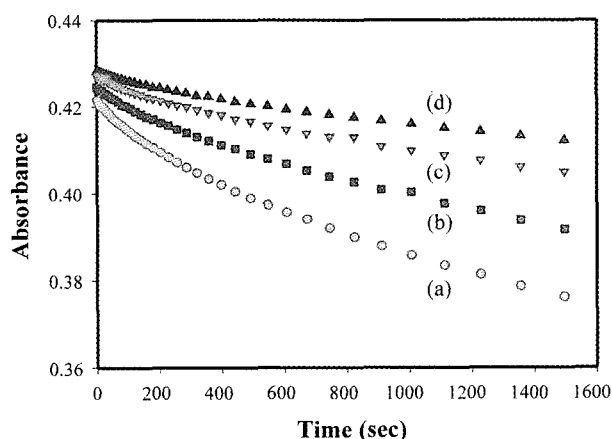


Figure 8. The decaying behavior of the absorbance of the poly(vinyl cinnamate) doped with compound 2 with the different irradiation time of 275 nm UV light. (a) 0 min (sample IV), (b) 5 min (sample V), (c) 10 min (sample VI), and (d) 15 min (sample VII).

which were measured from Figure 8 using the single exponential decay function (1). It is manifested that the merocyanine form of compound 2 in the film state becomes more stable and gets much smaller decaying rate (k) as the irradiation time at 275 nm increases, resulting in higher degree of crosslink formation.

When we vary the concentration of bifunctional dye in PVCi ranging from 1 to 20 wt%, the stability is improved significantly in each sample under same irradiation dose (see Figure 9). It is observed that the film sample doped with a higher concentration of the compound 2 would become more stable. Therefore, higher degree of photocrosslink in PVCi and bifunctional dyes (compound 2) provides higher steric hindrance to reduce the free volume for Z/E transformation and retard the reverse reaction to pristine spiropyrans.

Finally, in order to investigate the holographic properties of the photochromic materials, we monitored the diffraction efficiency measured by laser interference method. At 830 nm wavelength of diode probe beam, film samples have no

Table II. Calculated Parameters from the Decaying Behavior of Absorbance at 560 nm. *sample: PVCi doped with compound 2

Sample ^a	k (sec ⁻¹)
sample IV ^b	0.001256
sample V ^b	0.001087
sample VI ^b	0.000978
sample VII ^b	0.000896

^aDye conc. 5 wt%.

^bIrradiation time at 275nm: 0(sample IV), 5(sample V), 140(sample VI), 15(sample VII) min.

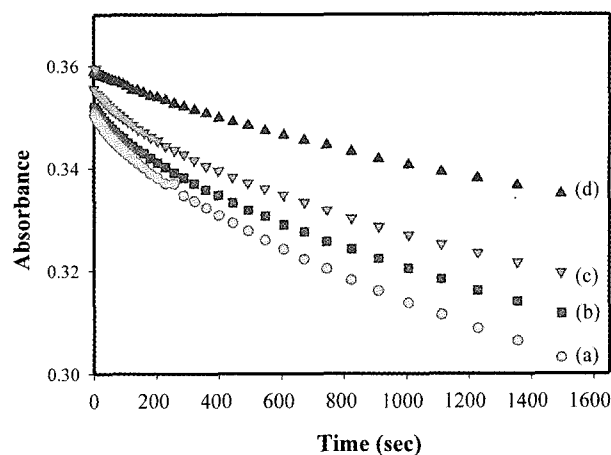


Figure 9. The decaying behavior of the absorbance of the poly(vinyl cinnamate) doped with compound 2 with the different dye concentration. (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, and (d) 20 wt%.

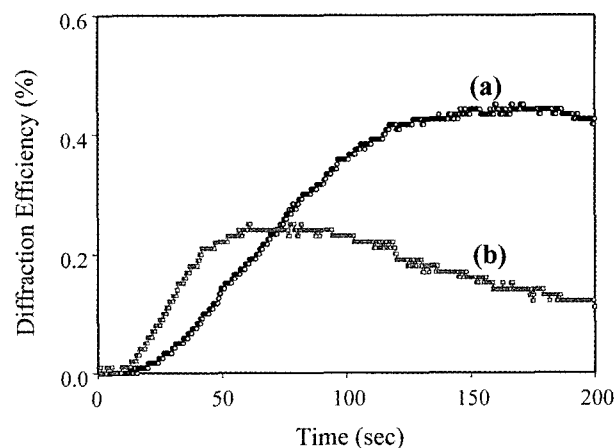


Figure 10. Dynamic behavior of the diffraction efficiency of the photochromic samples. (a) sample I and (b) sample III.

absorbance at all. The sample bearing the bifunctional dye (compound 2) was also irradiated under 365 nm (5 min) and 275 nm (15 min) sequentially for inducing photochromism and photocrosslinking. We irradiated UV light to reach the saturation of the photochromism and then, we fabricated the diffraction grating using 514 nm coupled laser lights. From this experiment, we can evaluate the stability of the photochromism observing the diffraction efficiency. In Figure 10, we can clearly observe that the sample III showed much lower diffractive performance than the sample I. This indicates that the photochromism of the sample III is much more stable than the sample I, which is attributed to the formation of photocrosslink through cinnamoyl moieties.

Currently, we make some efforts to study the stability of photochromism of the main-chain cinnamoyl polyester doped with bifunctional dye.

Conclusions

To improve the stability of the colored species of spirobenzopyran, we synthesized a new bifunctional dye containing spirobenzopyran and a cinnamoyl moiety. The effect of photocycloaddition between cinnamoyl moieties on the stability of the merocyanine of bifunctional dye was studied. The PVCi film doped with bifunctional dye exhibits highly improved stability of photochromism under irradiation of 365 and 275 nm monochromatic UV light sequentially.

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