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Photocoloration and photobleaching of 3-(2-adamantylidene)-2-[5-(*p*-diethylamino)phenyl-2-methyl-3-furylethylidene]-succinic anhydride doped in PMMA polymer film

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Abstract

The greenish fulgide **2-E** doped in PMMA polymer films was heated at various annealing temperatures. Upon irradiation with UV light (366 nm), fulgide **2-E** undergoes a conrotatory ring closure to the bluish colored closed form **2-C**. The later color was partially switched back to the original color when the films were irradiated with white light. The percentage conversion decreases with increasing the annealing temperatures. The observed large bathochromic shifts of λ_{max} for the opened and closed forms of **2** and the partial conversion of **2-C** to **2-E** were rationalized on the bases of electronic and steric effects. It was found that both isomers **2-C** and **2-E** absorb white light and under white light irradiation they interconvert and a photostationary state is reached. The kinetics of photocoloration and photobleaching processes were followed spectrophotometrically by monitoring the absorbance of the ring closed product **2-C** at its λ_{max} of 630 nm. The apparent first-order rate constants for both processes were determined. It was found that there was slight variation in rate constant for photocoloration reaction; which decreases with increase annealing temperature. On the other hand, the apparent rate constant of the photobleaching reaction increases with increasing the annealing temperature.

Keywords: Fulgides; Photochromism; Polymer film; Photobleaching, photocoloration, kinetics

1. Introduction

Photochromism of fulgides is a reversible photochemical electrocyclization. This 6π-electrocyclization is based on the reversible light-induced hexatriene/cyclohexadiene pericyclic reaction which is in accordance with Woodward–Hoffmann rules [1].

The development of a reversible optical information storage medium based on photochromic organic compounds has become a potential commercial reality since 1981. This is the result of the discovery by Heller and his group [2,3] of the first thermally irreversible photochromic fulgide, namely, (*E*)-3-isopropylidene-2-(2,5-dimethyl-3-furylethylidene) succinic anhydride. The thermal irreversibility of this compound is a result of introducing substituents other than hydrogen on the ring-closing carbons which prevents the hydrogen rearrangement and dehydrogenative aromatization side reactions [4]. Heller and Langan have also show that the thermal stability of fulgides was greatly improved when they contain a heteroatomic ring such as furyl, thienyl or pyrrolyl [5]. Indolylfulgides, mainly studied by Yokoyama and co-workers were found to have interesting photochromic properties [6–8]. Recently, photoinduced anisotropy properties such as dichroism and birefringence of fulgides and fulgimides have gained considerable attention. Control of these properties improves the optical properties and applications of photochromic fulgides [9–11]. Other properties of photochromic fulgides could also be controlled [12]. Organic photochromes such as fulgides have found potential applications in fields of optical storage memories [13], holographic recording [14], and multi-level recording [15]. The application of photochromic compounds in optical data storage or any other application will certainly be provided as films. This necessitates studying the photochromic performance of fulgides doped in or bounded to polymer matrices. In previous series of papers, we reported the photochromic properties of vacuum-deposited and polymer films of

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(*E*)-dicyclopropylmethylene-(2,5-dimethyl-3-furylethylidene)-succinic anhydride (**1-E**) (Scheme 1) [16–19]. Now we report the photochromic properties of 3-(2-adamantylidene)-2-[5-(*p*-diethylaminophenyl)-2-methyl-3-furylethylidene]-succinic anhydride (**2-E**) doped in polymethylmethacrylate (PMMA) polymer film at various annealing temperatures.

2. Experimental details

Fulgide **2-E** was prepared according to general procedure previously reported [20]. The films were prepared as follow: 2.23 g of PMMA (Aldrich product) was dissolved in 20 mL chloroform and warmed to ensure complete dissolution. The mixture was then cooled. Two blank films were prepared by taking 0.3 mL of the above solution and spread over a glass plate. These plates were covered and left overnight in the dark. To the remaining solution was added about 1 mg of fulgide **2-E** and mixed well. Then 0.3 mL of the mixture was added to each of the glass plates which then covered and left overnight in the dark. Two of these films were used without heating (room temperature, 20 °C), one was used to study the annealing effect and the other was used to follow the photochemical reaction. Another film was heated in the oven for 4 h at 60 °C and another two films were similarly heated for 4 h, one at 80 °C and the other at 100 °C. Ultraviolet and visible spectra were measured using Perkin-Elmer lambda EZ210 spectrophotometer. Photocoloration (366 nm) was carried out using Blak-Ray lamp model UVL-56 and photobleaching was obtained using a tungsten filament lamp and using a filter allowing only light with wavelength range of 500–1000 nm with intensity of 300 mW/cm^2 at the exposure zone.

3. Results and discussion

3.1. Effect of annealing

Upon heating the PMMA film at 100 °C for 4 h, several cracks appear on the film, this suggests such films should not be heated above this temperature as it is easily be removed. Fig. 1 shows the electronic absorption spectra of the films before and after annealing. The uv absorption spectra of fulgide **2-E** show two bands at λ_{max} 340 nm and 395 nm. It was found that no appreciable change in the absorption spectra of the unannealed and the annealed films of the peak at λ_{max} 395 nm. On the other hand, the peak at λ_{max} 340 nm deceases with increasing the annealing temperature.

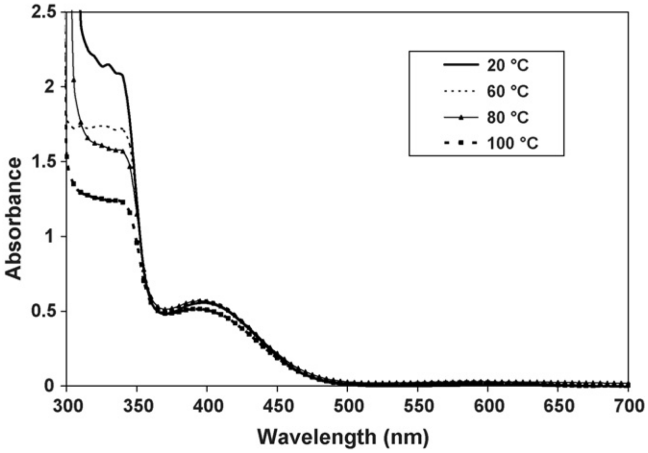
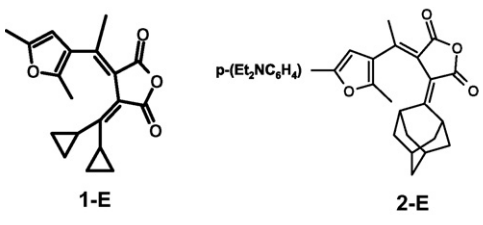


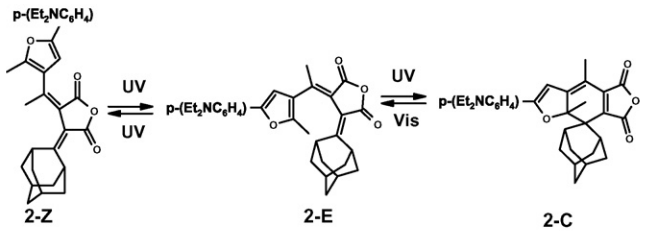
Fig. 1. The effect of annealing on PMMA films of fulgide **2-E**.

3.2. Photocoloration

Fulgide **2** was obtained as a greenish solid mixture of two geometrical isomers, the cis and trans isomers (**2-Z**, **2-E**). The pure **2-E** isomer was obtained as we described earlier [21]. The UV absorption spectra of fulgide **2-E** show two absorption bands at 340 nm and 395 nm. The introduction of the *p*-diethylaminophenyl group into the 5-position of the furan ring shifts the absorption spectra to longer wavelengths of both open and closed forms of fulgide **2** (**2-E**, **2-C**) compared to fulgide **1** (**1-E** (λ_{max} 300 nm and 360 nm), **1-C** (λ_{max} 518 nm)). This large bathochromic shift is due to the electron donating ability of the *p*-diethylaminophenyl group which increases the conjugation through the system [8]. Both isomers absorb UV light and only the **E**-form undergoes a conrotatory photocyclization upon irradiation with UV light (366 nm) to give 7,7a-dihydro-7,7-(2-adamantyl)-2-(*p*-diethylamino)phenyl-4,7a-dimethylbenzo[*b*]furan-5,6-dicarboxylic anhydride **2-C** as a blue color with absorption maximum at λ_{max} 630 nm (Scheme 2). The absorption maximum of **2-C** in toluene solution appeared at λ_{max} 610 nm. Such red shift in going from toluene to PMMA is expected, because it is known that polar medium shifts the absorption spectra of the colored form to longer wavelengths [4,22]. Since upon UV irradiation all the three isomers absorb, a photostationary state will soon be reached. The rate of each step will depend on its quantum yield and the intensity of absorbed light [23]. The unannealed and annealed films of fulgide **2** were irradiated with mercury lamp (366 nm) and the photocoloration process was followed



Scheme 1.



Scheme 2. Photochemical reactions of fulgide 2.

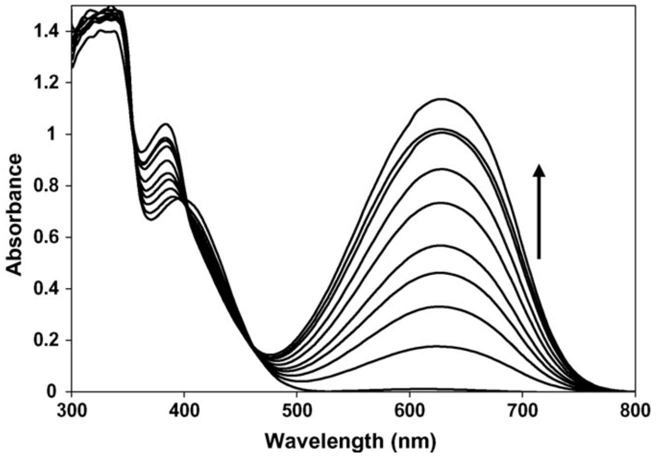


Fig. 2. Absorption spectra of photocoloration of fulgide **2-E** polymer film annealed at 60 °C. The arrow direction indicates the increase of absorbance with increasing exposure time.

spectrophotometrically by monitoring the absorption of the cyclized product **2-C** at its $\lambda_{\max}$ of 630 nm at intervals of time. Fig. 2 is a representative sample showing the spectrum of the photocoloration of the annealed film of fulgide **2** at 60 °C.

Kinetics of fulgides shows in general first-order rate dependence, especially in solutions [24–26]. However, in polymer matrices deviation from simple first-order reaction was observed. Such nonlinearity of the first-order plots was attributed to several factors such as the effects of the polymer matrix on the photochromic compound, the presence of more than one conformers or the dye might be confined in the solid polymer matrix [27–30].

The integrated form of the first-order rate law for the photocoloration process is:

$$\ln\frac{A_\infty - A_0}{A_\infty - A_t} = kt$$

where k is the rate constant, A_∞ is the absorbance of the cyclized product **2-C** at infinite time, A_0 the absorbance at zero time and A_t is its absorbance at time t. Plot of $[\ln(A_\infty - A_0)/(A_\infty - A_t)]$ against time, gives one straight line with slope equals k. Fig. 3 shows the first-order plots for the photocoloration of fulgide **2-E** polymer films annealed at different temperatures. We have previously found that plot of $[\ln(A_\infty - A_0)/(A_\infty - A_t)]$ against time for fulgide **1-C** doped in polystyrene polymer films, gives two straight lines with slopes k_1 and k_2 [19]. This was explained on the bases that there were two major conformers of fulgide **1-E**, which react in sequence. Similar results where found by Rappon [29]. Table 1 shows the apparent rate constants of photocoloration of fulgide **2-E** in toluene solution and PMMA polymer films at various annealing temperatures. As expected the photocoloration reaction is faster in toluene solution ($k = 0.0074\ \mathrm{s}^{-1}$) than that in PMMA thin films ($k = 0.0065\ \mathrm{s}^{-1}$ at 20 °C). It was found that the rate constants are slightly decreased with increasing annealing temperature.

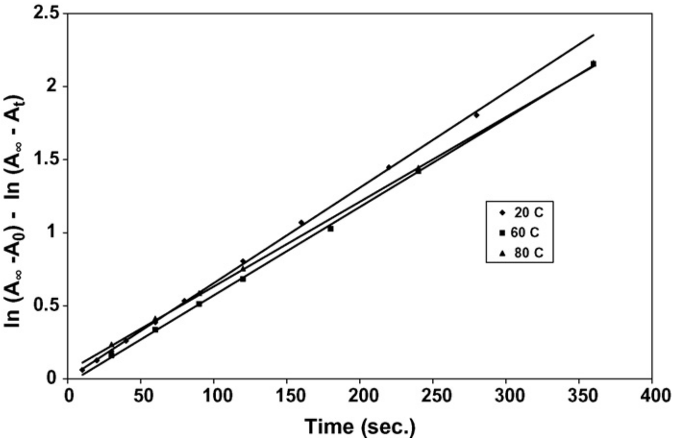


Fig. 3. First-order plot of photocoloration of fulgide **2-E** film at various annealing temperatures.

3.3. Photobleaching

When the closed ring form **2-C** was irradiated with white light, the blue color of **2-C** is gradually disappeared with time and fulgide **2-E** is regenerated. Fig. 4 shows the absorption spectrum of the photobleaching reaction of fulgide **2-C** doped in PMMA polymer film annealed at 60 °C. However, this conversion is not complete. Thus, while **1-E** shows almost complete conversion to the colorless open-form **1-C**, the adamantylidene fulgide **2-C** is only partially converted. Moreover, we found that the percentage conversion of the **C**-form to the **E**-form decreases with increasing the annealing temperature (Table 1). Interestingly, when a fresh PMMA film of **2-E** was irradiated directly with white light, it converted to the bluish closed form **2-C** until equilibrium is reached where no further change in absorbance was observed (Fig. 5). Thus both isomers **2-E** and **2-C** were interconverted upon irradiation with white light until a photostationary state is attained (Scheme 3). The low conversion of **2-C** to **2-E** upon irradiation with white light could be attributed to the two competing factors, the electron donating ability of the *p*-

Table 1

The forward and backward first-order reactions of fulgide **2-E** in toluene solution and PMMA polymer films at different annealing temperatures

Reaction	k_1 ($\times 10^{-3}\ \mathrm{s}^{-1}$)	(C → E) %conversion
Photocoloration of fulgide **2-E** in toluene solution at room temperature (20 °C)	7.4	
Photocoloration of fulgide **2-E** at room temperature (20 °C)	6.5	
Photocoloration of fulgide **2-E** annealed at 60 °C	6.0	
Photocoloration of fulgide **2-E** annealed at 80 °C	5.8	
Photobleaching of fulgide **2-C** in toluene solution at 20 °C	1.9	73.5
Photobleaching of fulgide **2-C** at room temperature (20 °C)	–	81.7
Photobleaching of fulgide **2-C** annealed at 60 °C	2.7	53.6
Photobleaching of fulgide **2-C** annealed at 80 °C	5.2	48.3
Photobleaching of fulgide **2-C** annealed at 100 °C	–	43.9

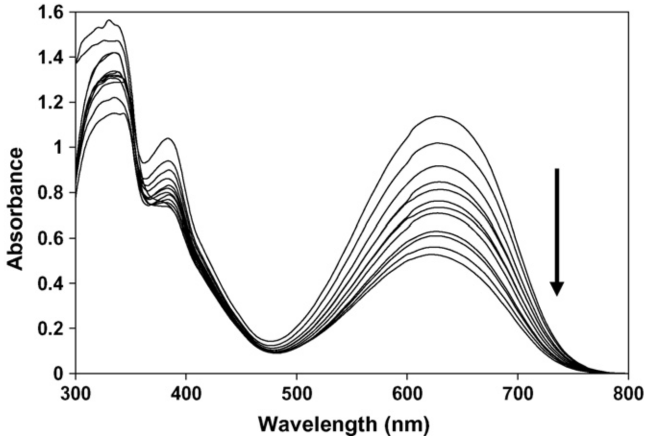


Fig. 4. Absorption spectra of photobleaching reaction of closed ring form **2-C** polymer film annealed at 60 °C. The arrow direction indicates the decrease of absorbance with increasing exposure time.

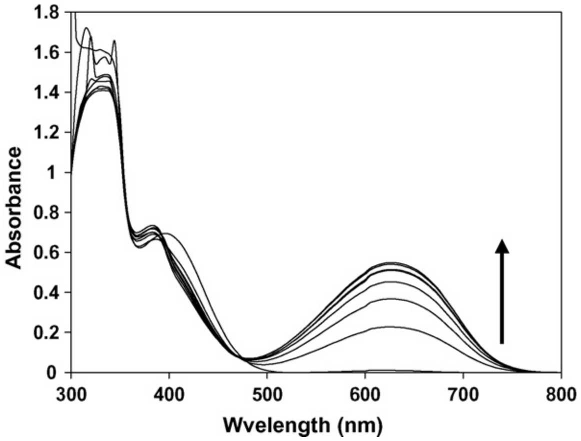
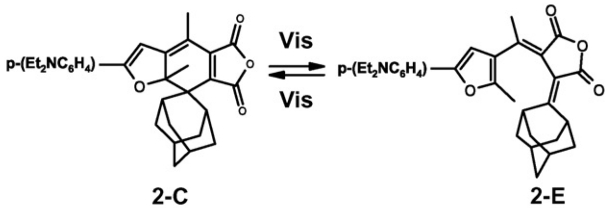


Fig. 5. Absorption spectra of photocoloration of fulgide **2-E** unannealed film irradiated directly with white light. The arrow direction indicates the increase of absorbance with increasing exposure time.

diethylaminophenyl group at the 5-position of the furan ring and the steric bulkiness of the adamantylidene group. The electron donating ability of *p*-diethylaminophenyl increases the conjugation through the system which leads to the stabilization of the ring-closed form **2-C**. and consequently decreases the quantum yield ($\Phi_{(CE)}$(Vis)) of the ring-opening reaction (bleaching) [4,8,31]. However, the steric bulkiness of the adamantylidene group increases the quantum yield ($\Phi_{(CE)}$(Vis)) of the ring-opening reaction (bleaching) due to the increased strain caused by the adamantylidene group on the cyclohexadiene ring of the **2-C** form [4,7,32]. It seems that the electronic factor controls the conversion process and thus leading to the low conversion of **2-C** to **2-E**.



Scheme 3.

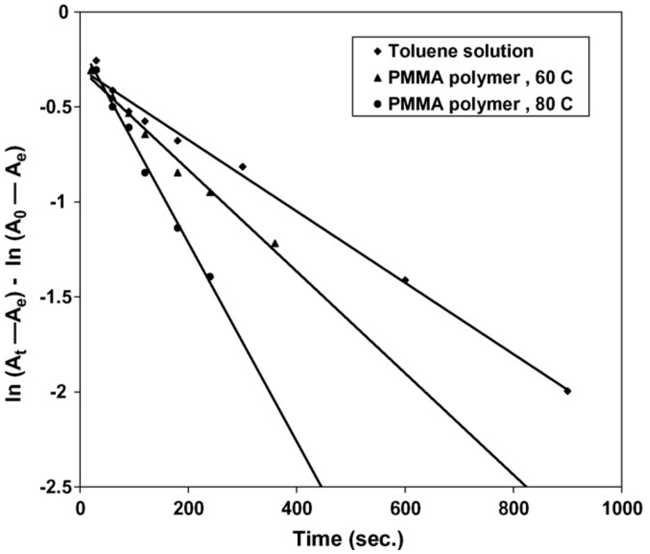


Fig. 6. First-order plot of the photobleaching reaction of closed ring form **2-C** in toluene solution and PMMA polymer films annealed at 60 °C and 80 °C.

Reaction rates of the photobleaching process were studied in solution and solid matrices below and above room temperatures [18,24–30,33]. At temperatures around and above room temperatures, photobleaching of the closed ring form **2-C** to the opened ring form **2-E** follows simple first-order rate equation. Since both isomers **2-C** and **2-E** absorb white light, a photostationary state will be reached. Then the integrated form of the reversible first-order rate law for the photobleaching process is:

$$\ln\frac{A_t - A_e}{A_0 - A_e} = -kt$$

where k is the rate constant, A_0 the absorbance of the cyclized product **2-C** at zero time and A_t is its absorbance at time t and A_e is its absorbance at equilibrium (photostationary state) at the end of the reaction. Plot of $[\ln(A_t - A_e)/(A_0 - A_e)]$ against time, gives a straight line with a slope equals to ($-k$). Fig. 6 shows the first-order rate plots of the photobleaching reaction of fulgide **2-C** polymer film at different annealing temperatures and Table 1 summarizes their apparent rate constants. From Table 1 it is obvious that the reaction rate for the photobleaching process is slower than that of the photocoloration process. It is also evident that the rate of photobleaching decreases with increasing annealing temperature.

4. Conclusion

The photochromic properties of the greenish fulgide **2** doped in PMMA polymer film at various annealing temperature were investigated. Upon irradiation with UV light (366 nm), fulgide **2-E** undergoes a conrotatory ring closure to the bluish colored closed form **2-C**. The later color was partially switched back to the original color when the films were irradiated with white light. The percentage conversion decreases with increasing the annealing temperatures. The observed large bathochromic shifts of λ_{max} for the opened and closed forms of **2** was attributed to the electron donating ability of the *p*-diethylaminophenyl substituent which elongate the conjugation system. The partial conversion of **2-C** to **2-E** was rationalized on the bases of electronic and steric effects. It was found that both isomers **2-C** and **2-E** absorb white light and under white light irradiation they interconvert and a photostationary state is reached. The kinetics of photocoloration and photobleaching processes were followed spectrophotometrically by monitoring the absorbance of the ring closed product **2-C** at its λ_{max} of 630 nm. The apparent first-order rate constants for both processes were determined. It was found that there was slight variation in rate constant for photocoloration reaction; which decreases with increase annealing temperature. On the other hand, the apparent rate constant of the photobleaching reaction increases with increasing the annealing temperature.

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