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Photoreactions of spirophenanthrooxazine dispersed in polystyrene film at room temperature

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Abstract

The properties of photomerocyanine (PMC) form of spirophenanthrooxazine (SPO; 1,3-dihydro-1,3,3-trimethyl-spiro[2*H*-indol-2,3′-[3*H*]-phenanthr[9,10-b][1,4]oxazine]) dispersed in polystyrene (PS) have been studied by photobleaching technique at room temperature. Upon visible irradiation, absorbance in the visible region decreases and ΔOD spectrum varies with laser wavelength, intensity, irradiation time and sequence of photoirradiation. Experimental results indicate that open forms of SPO experience not only the photobleaching reaction to SPO but also the photoisomerization reaction to another open form and at least three PMC isomers of SPO are involved in the photoreaction. Furthermore, thermal isomerization reaction between PMCs and thermal SPO → PMC reaction have been also observed at room temperature.

Keywords: Spirophenanthrooxazine; Photomerocyanine; Photobleaching

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1. Introduction

Spiropyrans (SPs) and spirooxazines (SOs) have been intensively investigated over many years [1–21] because of the wide application potential, e.g. in ophthalmic lenses and in optical memory device [1–4]. Among spirocompounds, SOs are of particular interest due to their relatively high fatigue resistance [2,5,6]. Upon UV irradiation, SO, whose indoline ring is nearly orthogonal with respect to the oxazine ring, experience cleavage of spiro C–O bond of oxazine ring and then, two parts of the molecule rotate to form their planar photomerocyanine (PMC) (Scheme 1) [1,2,5,6]. Depending on the configurations about the three partial double bonds between the two rings at each end, eight PMC isomers are possible. Among them, only four conformers with the central transoid segment are supposed to contribute to the equilibrium mixture at room temperature [7–10]. When the light is removed, PMC tends to revert thermally toward SO in order to reach its original stationary state [6,11,12].

The transient absorption and time-resolved Raman studies of spironaphthooxazine (SNO) indicated that the cleavage of the spiro C–O bond is very efficient [11–13] and the overall photocoloration reaction takes place in approximately picosecond range [9,14,15]. Recent photobleaching experiment of SNO dispersed in polystyrene (PS) [16] showed that the reaction intermediate, whose spectrum is in close resemblance with the transient absorption spectrum of SNO and its related spirocompounds [17–19], is trapped at 25 K.

Because the equilibrium constant of SNO $\rightleftarrows$ PMC is $\sim 10^{-4}$ [12], the ground state equilibrium is on the side of the closed form and PMC reverts almost completely into SNO after the cessation of UV irradiation. However, the equilibrium constant of spirophenanthrooxazine (SPO; 1,3-dihydro-1,3,3-trimethyl-spiro[2*H*-indol-2,3′-[3*H*]-phenanthr[9,10-b][1,4]oxazine]), which has one more phenyl ring in the oxazine part than SNO does, is about two orders of magnitude larger than that of SNO at room temperature [12]. Because PMC form of SPO gives large enough absorbance in the visible region at room temperature, the photobleaching experiment of PMC form can be performed without a prior UV irradiation that may complicate the system.

In this paper, photochemical and photophysical properties of PMC form of SPO doped in PS film were studied by photobleaching technique at room temperature. We examined especially how the absorption spectrum is affected by light intensity, wavelength and the sequence of the photoirradiation. Evidences for the photoreaction between PMCs and for the thermal reaction of SPO to PMC are provided.

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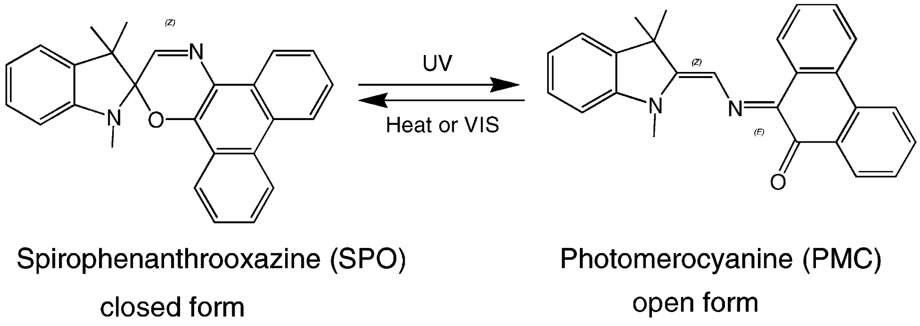

Scheme 1. Photochromism of SPO.

2. Experimental

SPO was purchased from Aldrich and used without further purification. PS and spectrograde toluene were purchased from Aldrich. Thin PS films containing 10% SPO (SPO/PS) were prepared from toluene by solvent-cast method. Sections of the film ~170 μm thick were cut from the dried film and mounted in a sample holder. The photobleaching experiments were performed using a red He–Ne laser (Laser Research, 632.8 nm), a yellow He–Ne laser (Uniphase 1667, 594 nm) and a green laser diode (LeadLight Technology GLM-1, 532 nm). The light irradiation time and intensity were controlled using a mechanical shutter (Uniblitz T132) and neutral density filters, respectively. Then the absorption spectra of the sample were measured using a UV–VIS spectrophotometer (Shimadzu 2100S), which is interfaced to an IBM compatible PC.

3. Results and discussion

The extent of the π-system of PMC form of SPO seems to be related not only to its relatively high equilibrium constant for the thermochromic reaction but also to its significant absorbance in the visible region. For instance, Fig. 1 indicates that at room temperature absorbance of 10% SPO/PS reaches about 1.2 at the absorption maximum (λ_{max}) in the visible region and therefore, it is possible to directly perform the photobleaching experiment on the PMC form without a prior UV irradiation.

Fig. 2 represents how the ΔOD spectra (the difference in the absorbance between the post- and pre-irradiation) of SPO/PS are affected by the photobleaching reaction. The wavelengths of the irradiation beam (λ_L) are 594, 632.8 and 532 nm, respectively. The ΔOD spectra in Fig. 2(A)–(C) are similar in general and the centroid of absorbance decrease, which we denote here as 'dip', is located near at λ_{max}. When the sample additionally exposed to the intenser beam, the dip rapidly grows and becomes similar to the upside-down of the absorption spectrum. The integrated absorption area in the visible region somewhat decreases regardless of the irradiation wavelength. Because the absorption in the visible region is related only with open forms, the result implies that most species absorbing either 632.8, 594 or 532 nm light experience the photochemical PMC → SPO reaction.

Fig. 3 represents dependence of ΔOD spectra on λ_L. Here, (a), (b) and (c) correspond to (b) in Fig. 2(C), (d) in Fig. 2(A) and (d) in Fig. 2(B), respectively, and are adjusted to the same intensity at the dip maximum. The dip maximum is located at ~590 nm both in (a) and (b), while at ~602 nm in (c). The red-tail parts of the dip in (a) and (b) almost overlap each other although difference of the laser wavelengths used is 62 nm. However, relative intensity of the dip at ~550 nm region is larger in (a) compared with (b). Meantime, the red-tail part of (c) is displaced by ~10 nm to the red compared with those of (a) and (b). From these observations, it is deduced that the species responsible for the dip at ~550 nm is different from that responsible for the dip at ~590 nm and that there exists another species that experiences substantial photoreaction only by 632.8 nm light. This implies that the absorption band in the visible region is inhomogeneously broadened by at least three open forms, each of which is

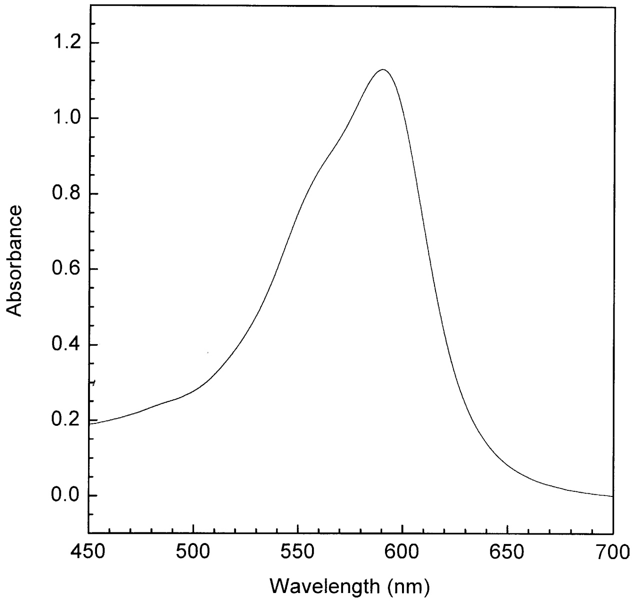

Fig. 1. Absorption spectrum of 10% SPO/PS at room temperature.

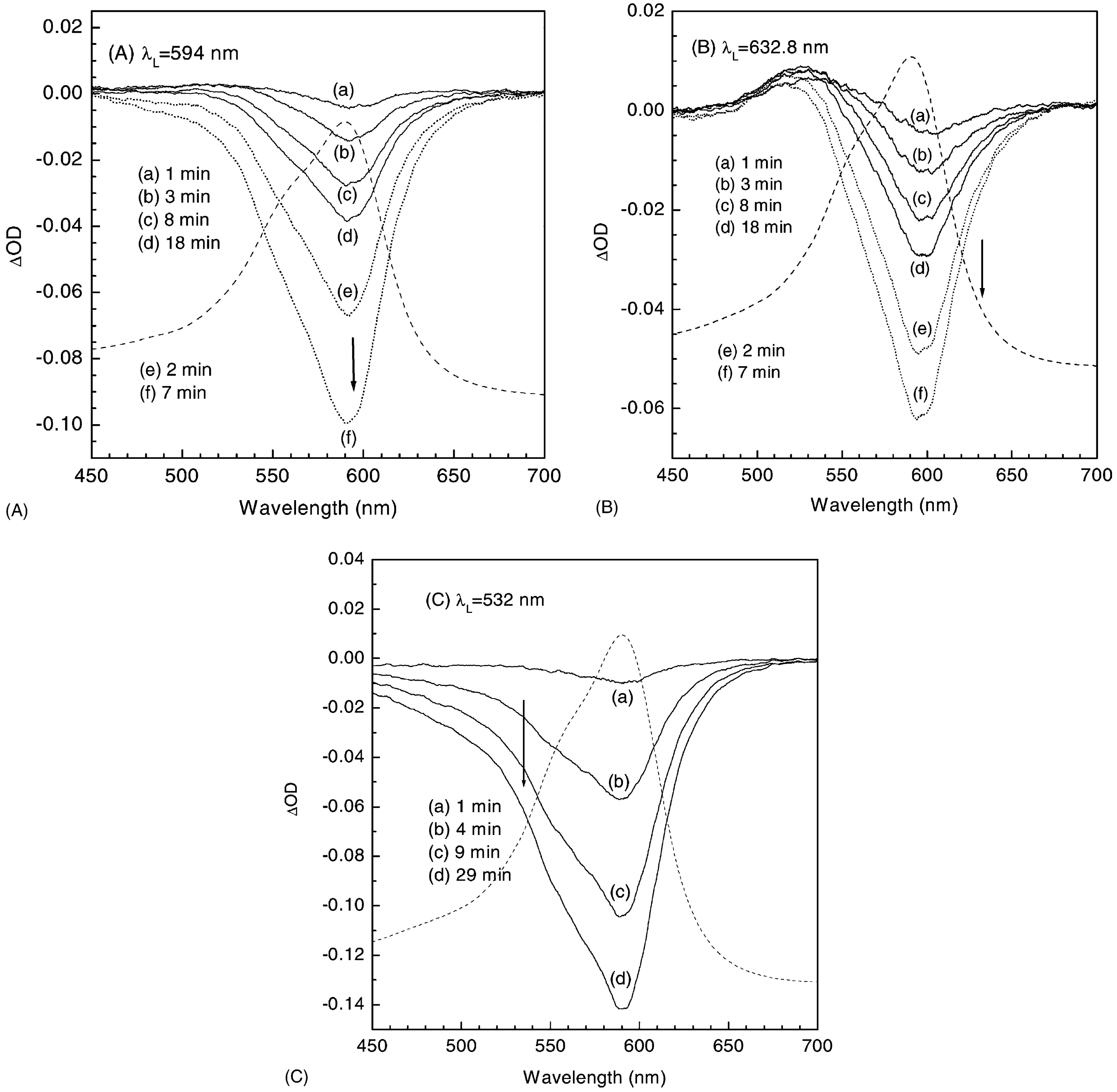

Fig. 2. ΔOD spectra of SPO/PS obtained at room temperature by the photobleaching experiment. The arrows indicate the wavelengths of the light: (A) $\lambda_L = 594$ nm; (B) $\lambda_L = 632.8$ nm; (C) $\lambda_L = 532$ nm. The solid lines correspond to the photobleaching with the weak beam: (A) 0.8 mW/cm^2; (B) 4.0 mW/cm^2; (C) 24 mW/cm^2. The dotted lines correspond to the additional irradiation using 10 times intense radiation.

mainly responsible for the dip at ∼550, 590 and >600 nm, respectively. Although it is difficult to tell the exact position of λ_{max} of each species because of the unresolved absorption spectrum, we will denote them as PMC$_{550}$, PMC$_{590}$ and PMC$_{>600}$, respectively.

Contrary to the decrease in the absorbance observed in most visible regions, Fig. 2(B) shows that the absorbance at ∼535 nm is slightly increased. Especially, (a) and (b), obtained at the early stage of the irradiation, show that the total absorbance in the visible region is nearly conserved. This result seems to indicate that at the initial stage of the irradiation the species absorbing 632.8 nm light nearly stoichiometrically transforms into another species absorbing at ≤580 nm. Because the absorption band in the visible region is related with the open forms, it is evident that there is a reaction path for a photoreaction between open forms and that the thermal isomerization reaction between PMCs of SPO is slow even at room temperature. This is interesting result

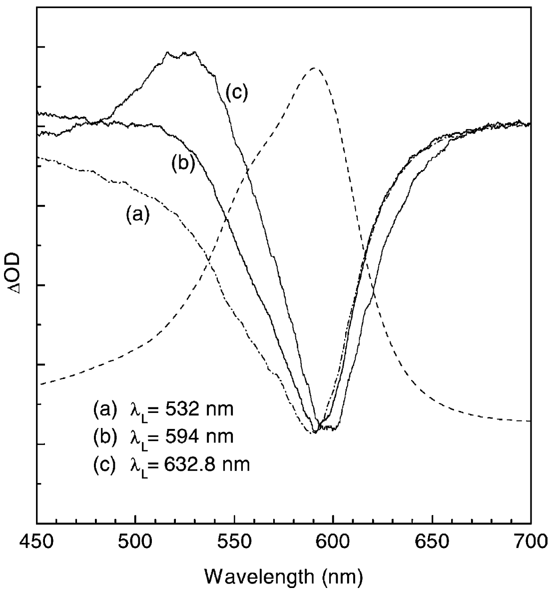

Fig. 3. Dependence of ΔOD spectra on λ_L: (a) $\lambda_L = 532$ nm; (b) $\lambda_L = 594$ nm; (c) $\lambda_L = 632.8$ nm. The *y*-axis scale has been adjusted in order that each ΔOD spectrum may have same intensity at the dip maximum.

because photoisomerization reaction between PMCs is observed for not many spirocompounds and at only low temperatures so far [20,21]. As the irradiation time gets longer, the integrated absorption area decreases and the center of the absorbance increase in the ΔOD spectra appeared to be blue-shifted. From these results, it is deduced that the maximum position of the absorption gain locates to the red of 535 nm when it is not interfered with the dip and therefore, the species responsible for the absorbance gain near at 535 nm may correspond to PMC_{550}. It is also possible that PMC_{590} is produced by 632.8 nm light although its evidence has not been obtained probably due to the interference between absorption gain and dip.

Meanwhile, the intensity of the absorption gain becomes smaller with decrease in λ_L and therefore, only the trace of absorption gain is observed for $\lambda_L = 594$ nm (Fig. 2(A)) and no gain for $\lambda_L = 532$ nm (Fig. 2(C)). These results may be explained using one of followings. (1) The presence of specific open form, which photochemically transforms by the light at $\lambda > 600$ nm into PMC absorbing at ∼535 nm. This implies that only $PMC_{>600}$ can experience the photoreaction. (2) The interplay between the negative-going dip and positive-going absorbance gain. Because the λ_L in Fig. 2(B) is far apart from 535 nm, the absorbance gain is less interfered with the dip and therefore, the absorbance gain remains even for the prolonged irradiation time. However, because λ_L in Fig. 2(A) is close to the absorption band of the species produced by the photoreaction, it may be bleached immediately on its production. Therefore, the interference between the absorbance gain and the dip may result in a trace of gain in the initial ΔOD spectra. Because the irradiation beam bleaches PMC_{550} first for the Fig. 2(C), a dip will be obtained at ∼550 nm. The absorbance gain will be located at ∼590 nm (or >600 nm) region if there is a reaction path for the photochemical $PMC_{550} \rightarrow PMC_{590}$ (or $PMC_{>600}$). However, because the amount of PMC_{550} is very small, it may be difficult to obtain the observable absorption increase. Because of the limited experimental data, it is not certain at this moment which one better describes the experimental data.

Fig. 4(A) shows the results of subsequent photobleaching of (f) in Fig. 2(A) with 632.8 nm light. The ΔOD spectra obtained with weak beam indicate that the absorbance in 500–620 nm range increases and maximum gain is observed at 585 nm and a shoulder at 550 nm. As the photobleaching continues, the maximum slowly shifts toward 580 nm. However, the ΔOD spectra obtained with intenser laser beam are totally different due to the increase in the photobleaching rate. Because of the rapid growth of a dip at >600 nm, the maximum position of the absorption gain shifts toward 525 nm as the irradiation continues. Meanwhile, the dip at 630 nm slowly shifts toward 602 nm and, at the same time, evolves into the one having intricate structure at 570–620 nm. Because the intricate structures is also observed in 570–610 nm region of the Fig. 2(B), it is deduced that it corresponds to the vibronic structure of the species experiencing the photoreaction by the light at 632.8 nm rather than to the noise. Although the natures of the chemical species are ambiguous due to the limited experimental data, it is plausible to attribute $PMC_{>600}$ to the species representing the intricate structure. The 632.8 nm light at a given intensity seems not to stimulate the photoreaction of PMC_{550}.

Fig. 4(B), which is quite different from Fig. 4(A), represents the results of the subsequent photobleaching of (f) in Fig. 2(B) with 594 nm light. Here, the photobleaching is performed in the reverse order to Fig. 4(A). In the photobleaching with weak beam, a broad and shallow dip is produced near at 530 nm while the absorbance near at 600 nm increases significantly. The integrated absorption area is increased during the photobleaching process and ΔOD spectra resemble the upside-down of (f) in the Fig. 2(B). As the irradiation time and intensity increase, the dip shifts toward 550 nm, another distinct dip at ∼590 nm rapidly grows and the intensity of the absorbance gain gradually decreases. These results indicate that the laser beam depletes the two kinds of PMCs, which have absorption maximum at ∼550 nm (PMC_{550}) and ∼590 nm (PMC_{590}), respectively. In fact, because 590 nm is closer to λ_L than 550 nm and the PMC_{590} is more abundant than PMC_{550}, the photobleaching rate of PMC_{590} is larger than that of PMC_{550}.

A characteristic common to the Fig. 4(A) and (B) is the substantial increase in absorbance at the initial stage of the photoirradiation. This fact seems somewhat unusual at a glance because the visible irradiation on PMC leads to the increase in the absorbance in the visible region. However, by considering the thermal non-equilibrium state, this can be interpreted as follows: if the species is exposed to 632.8 nm light first, most of PMC absorbing the light may convert into

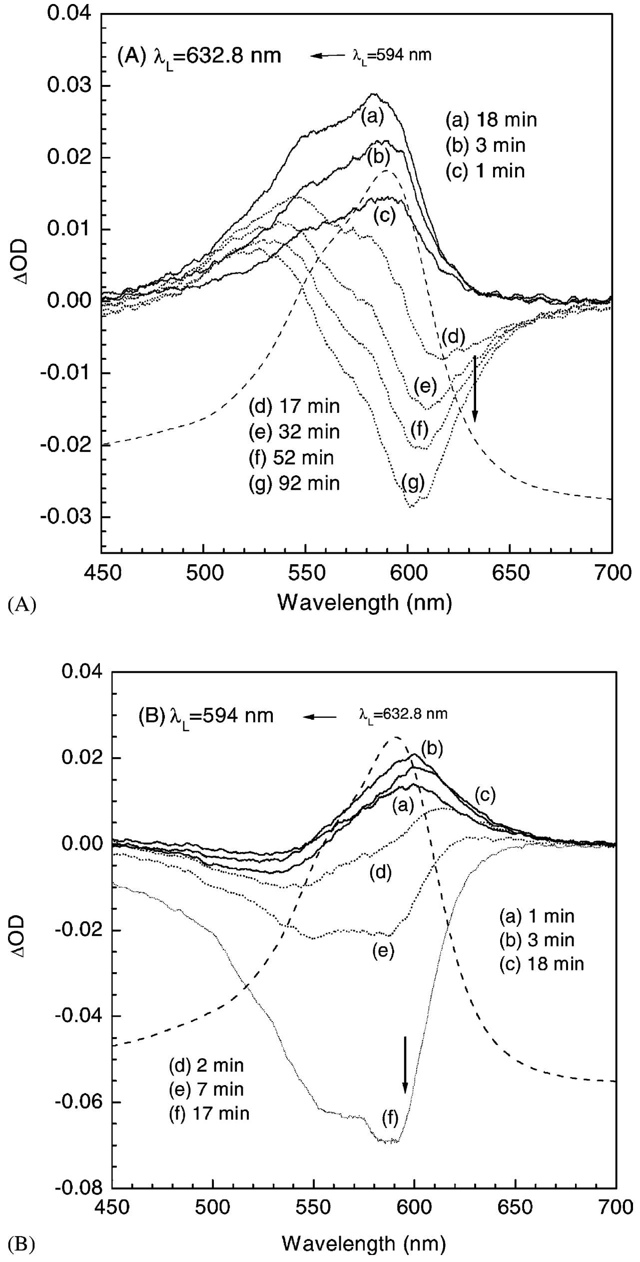

Fig. 4. ΔOD spectra obtained by the subsequent photobleaching with different wavelengths. The arrows indicate the wavelengths of the second beam: (A) photobleaching of (f) in Fig. 2(A) with 632.8 nm light; (B) photobleaching of (f) in Fig. 2(B) with 594 nm light. The solid lines correspond to the photobleaching with the weak beam: (A) 4.0 mW/cm^2; (B) 0.8 mW/cm^2. The dotted lines correspond to the additional irradiation using 10 times intense radiation.

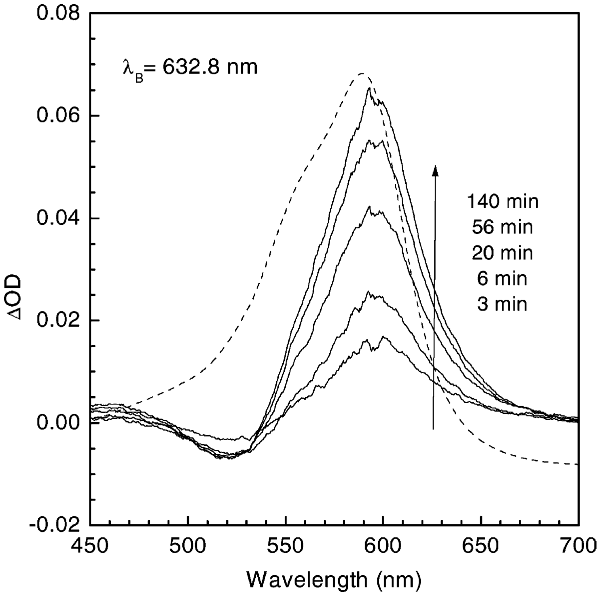

Fig. 5. ΔOD spectra as a function of elapsed time after terminating the photobleaching with 632.8 nm light. The sample was irradiated for 3 min at the intensity of 40 mW/cm^2. The dashed line depicts the absorption spectrum in an arbitrary scale.

SPO and part of them into the another PMC isomer. At the moment the light is removed, the system is away from the equilibrium state and therefore, the system will thermally move toward the original state to produce more PMC$_{550}$, PMC$_{590}$ and PMC$_{>600}$. Although the system is exposed to 594 nm light at this point, the thermal SPO → PMC reaction still dominates over either the photochemical PMC → SPO reaction or isomerization reaction between the two PMCs as long as the intensity of the second beam is weak enough as used in this study. Therefore, the original absorption spectrum will be restored and the ΔOD spectrum becomes similar to the upside-down of (f) in Fig. 2(B). Fig. 5, which represents the ΔOD spectra as a function of elapsed time after terminating the photoirradiation with 632.8 nm light, justifies the interpretation. This result is somewhat interesting because the thermal PMC → SP (or SO) reaction is the one frequently observed for the positive photochromic spiro-compound. Meanwhile, the bleaching near at ∼530 nm can be attributed to the thermal back reaction of PMC, which is photochemically produced by 632.8 nm light, to the original species. Similar explanations also can be applied to the case where the lights are irradiated in the reversed order.

In summary, the photobleaching reactions of SPO/PS system have been studied at room temperature. Open forms of SPO can experience not only the photobleaching reaction to SPO but also the photoreaction to another open form. Dependence of the ΔOD spectra on the irradiation time, intensity and wavelengths indicates that at least three PMC isomers of SPO are involved in the photoreaction. Among them, PMC$_{590}$ is the most abundant species in the PS matrix. Furthermore, thermal SPO → PMC reaction and isomerization reaction between PMCs have been observed at room temperature.

Acknowledgements

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