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# Thermal reactions of spironaphthooxazine dispersed in polystyrene film at low temperatures

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**Abstract**

The thermal behaviors of non-planar photoproduct X and photomerocyanine (PMC) form of spironaphthooxazine (SNO) dispersed in polystyrene have been studied using low-temperature absorption spectroscopy. Because the amount of X trapped in polymer is greatly influenced by temperature, ΔOD spectra vary with temperature. Although the reaction rate is extremely slow at 25 K, X experiences both the thermal bleaching reaction to SNO and thermal transformation to give at least three different PMC isomers. At 150 K, ΔOD spectra resemble upside-down of the absorption spectra in the visible region and the thermal bleaching reaction to SNO is the principal reaction.

*Keywords:* Spirooxazine; Thermal bleaching; Low temperature; Photomerocyanine

## 1. Introduction

Spiropyrans (SP) and spirooxazines (SO), which exhibit photochromic behavior, are potentially applicable as display system, optical memory device, optical switching device, ophthalmic lenses and non-silver high resolution photography [1–4]. Although the studies on their photophysical and photochemical properties, synthesis and applications have been extensively performed over past decades, a detailed mechanism of their photochromic and thermochromic reactions is still not fully understood due to the complexity of the system [1–24].

Among spirocompounds, SO are of particular interest due to their relatively high photostability [1,5,6]. Colorless SO experiences a reversible photochemical transformation upon UV irradiation to give their colored photomerocyanine (PMC). This involves heterolytic cleavage of C–O spirobond of oxazine ring followed by a rotation of two parts of the molecule to achieve coplanarity (Scheme 1) [1,2,5,6]. Then PMC tends to revert to SO either thermally or photochemically. Depending on the configurations about three partial double bonds between the two rings at each end, eight PMC isomers are possible. Since the cisoids are very unstable due to their steric hindrance [7,8], only transoids are supposed to contribute to the equilibrium mixture at room temperature. Because the relative stability of transoids, i.e., the relative amount of each isomer depends on the polarity of solvents [9–11], it is known that the absorption spectra vary with the solvents. For the case of spironaphthooxazine (SNO) in methanol-d$_4$, $^1$H-NMR nuclear overhauser effect measurements indicated that TTC (*trans–trans–cis*) is the most stable isomer for PMC form [12].

Until recently, non-planar nascent photoproduct X of SNO (1,3-dihydro-1,3,3-trimethyl-spiro[2*H*-indol-2,3′-[3*H*]naphth[2,1-b][1,4] oxazine]) has been detected only as a transient species [13,14]. Transient absorption studies showed that upon UV irradiation the metastable species X having very broad absorption at 550–700 nm is instantaneously produced (∼700 fs) [13] and relaxes to their planar transoids at 2–12 ps [14]. Very recently, we observed that in the polymer matrix the absorption spectra of PMC at 25 K are very different from those obtained at 77–200 K with regard to broad absorption gains at 400–500 and 620–800 nm [11]. Upon visible irradiation, broad absorption decreases were initially observed on both the regions of the spectrum, while absorbance at around 530–600 nm increases. Because the species absorbing at both the tail parts of the absorption spectra are thermally unstable and the OD spectra at the early stage of the visible irradiation were similar to the transient absorption spectra of 6-nitro-spirobenzopyran [15,16], the species were attributed to the reaction intermediate X.

In this paper, we report the results of low-temperature UV/Vis absorption measurements of SNO dispersed in polystyrene (PS) film. Because X is not stable at room temperature and the thermal reaction of X is interfered

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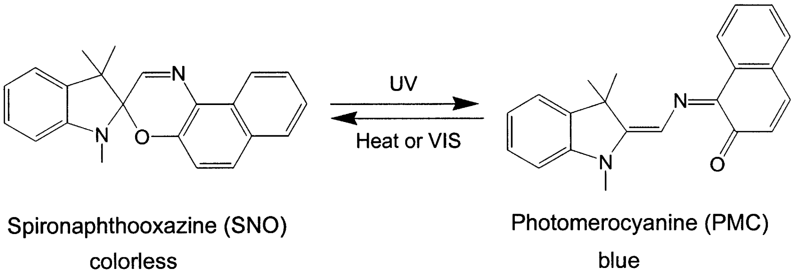

Scheme 1.

with the photoreaction of the various isomers of SNO in the presence of light, a low-temperature spectroscopy has been employed in the dark condition. A clear evidence for the thermal transformation of X to three PMC isomers is provided and the potential energy surface along the reaction path in the ground electronic state is proposed.

## 2. Experimental

SNO was purchased from Tokyo Kasei Industry and used as received. PS and spectroscopic grade toluene were purchased from Aldrich. Thin PS films containing 3% of SNO (SNO/PS) were prepared from toluene by solvent-cast method. Sections of the film were cut from the dried film and mounted in a variable temperature cryostat (Janis RGD-210). Prior to the UV irradiation, the sample was kept for 30 min at the desired temperatures, which is adjusted to within ±0.1 K using a temperature controller (Lakeshore Model 330). The photocoloration of SNO was achieved with 337 nm laser pulses from a $N_2$ laser (Laser Photonics LN-1000) at the desired temperatures. Then the absorption spectra of the sample were measured as a function of time after the cessation of the UV irradiation using a UV/Vis spectrophotometer (Shimadzu 2100S), which is interfaced to IBM compatible-PC.

## 3. Results and discussions

SNO are transformed into PMC form by heating or UV irradiation. Because the ground state equilibrium is shifted to the colorless form, PMC revert almost completely back to SNO in the dark. The rate of the thermal back reaction depends to a great extent on the temperature and it is generally known that the reaction finally stops at around −60 °C [1]. In the polymer matrix, the absorption spectra of SNO/PMC couple after the UV irradiation at 25 K are very different from those obtained at 77–200 K [11]. The results of the photobleaching experiment of PMC/PS and the dependence of the absorption spectra of SNO/PMC couple on the solvent polarity indicated that the absorption peak at 605 nm and the shoulders at 570 and 530 nm are due to three different transoids, which we denote here as $PMC_{605}$, $PMC_{570}$ and $PMC_{530}$, respectively. And it also suggested that the species responsible for a shoulder at 485 nm and the broad absorption tail on the red side of the absorption band is non-planar photoproduct X.

Fig. 1(A) shows how the thermal cycle has an influence on the absorption spectrum of SNO/PS. The curve (a) represents the absorption spectrum of SNO/PS film after the irradiation with UV at 25 K. When the sample described by curve (a) experiences thermal cycle (25 K → 77 K → 150 K → 25 K), the absorption spectrum gradually changes to (b), (c) and (d). With increasing temperatures, the absorbances on the both tail parts of the absorption band significantly decrease, while the absorbance on the peak and the shoulders increase. In contrast, the absorbance change is relatively small over the absorption band in the visible region with decreasing the temperature.

The difference between the neighboring absorption spectra are presented in Fig. 1(B). Gradual heating from 25 to 77 K causes the absorption increase at 600, 570 and 530 nm and the absorption decrease at 485 nm and at around 675 nm. This result is interpreted as that X thermally relaxes to at least three different transoids, $PMC_{605}$, $PMC_{570}$ and $PMC_{530}$ by completing the rotation around the central partial double bond between the two rings. The difference spectrum (b) − (a) also indicates that the integrated absorption area is slightly decreased. Because transoids associated with the longer chromophoric chain exhibit greater extinction coefficients than SNO or X, complete conversion from X to PMC should cause the increase in the total integrated absorption. Therefore, the results imply that part of X and/or some of PMC experiences thermal back reaction to give SNO during the temperature change. The curve (c) − (b) indicates that additional heating from 77 to 150 K causes the large absorption decrease on the both tail parts of the absorption band and leaves trace of production of $PMC_{605}$, $PMC_{570}$ and $PMC_{530}$. From the comparison of (b) − (a) and (c) − (b), it is deduced that X absorbing at longer wavelength is less stable than X absorbing at shorter wavelength. The curve (d) − (c), absorbance change of PMC/PS caused by the gradual cooling from 150 to 25 K, is typical type for the narrowing of the absorption band.

Fig. 2 shows the absorption spectra as a function of elapsed time after the cessation of UV irradiation at 150 K. The fact that the thermal bleaching reaction of PMC is still

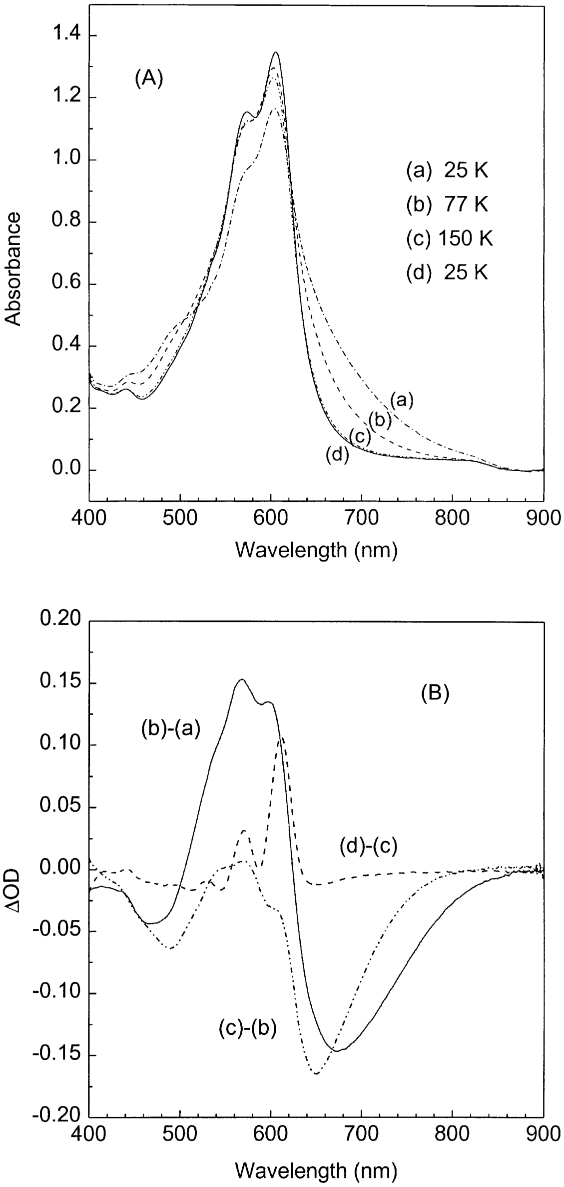

Fig. 1. Absorption (A) and ΔOD spectra (B) of PMC/PS. UV irradiation was performed with 337 nm pulses from the $N_2$ laser: (a) after UV irradiation at 25 K; (b) warmed to 77 K; (c) warmed to 150 K; (d) re-cooled to 25 K. The curves (b) − (a), (c) − (b) and (d) − (c) are difference spectra.

in progress even at 150 K when doped in PS is in contrast to that observed in solution, where the thermal bleaching reaction is known to stop at −60 °C [1]. Because the spectral shape is maintained during the thermal reaction, the rate of the thermal bleaching reaction seems to be similar for all PMC isomers. Therefore, the difference spectrum between at arbitrary elapsed times and at zero elapsed time is expected to be similar to the upside-down of the absorption spectra and it is justified in the inset. Because the amount of X trapped in the polymer is negligibly small at 150 K, the significant reaction in progress is only the thermal conversion of PMC to SNO.

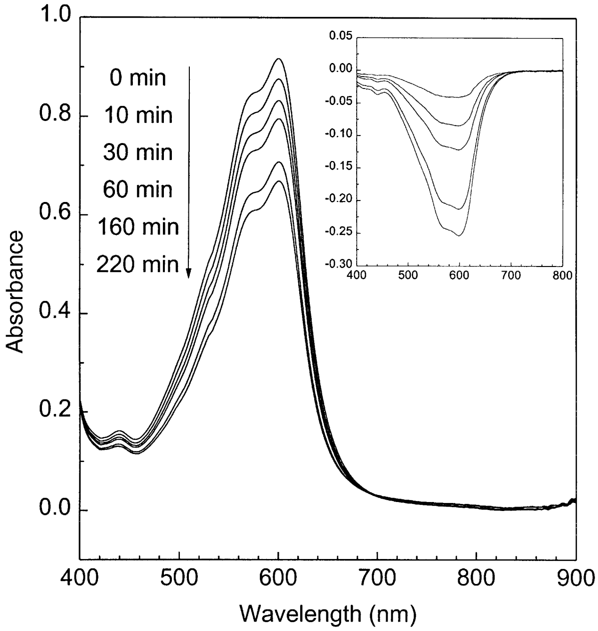

Fig. 2. Absorption of PMC/PS at 150 K in the dark as a function of elapsed time after UV irradiation. The inset shows ΔOD spectra.

Fig. 3(A) represents absorption spectra of SNO/PS as a function of elapsed time after the cessation of UV irradiation at 25 K. It shows that there is no significant change in the absorption spectra for a long time and most of X remains unchanged in the dark because of the extremely low thermal energy. However, the ΔOD spectra shown in Fig. 3(B) clearly indicate that certain types of extremely slow thermal reactions are still in progress. The results show that the absorbance increases at 500–620 nm and decreases at on both the tail parts of the spectra. And the half-life of X is roughly estimated as longer than 20 h at 25 K. We attribute X that experience the thermal reaction at 25 K, to the one coupled with local environment having especially high potential energy in the amorphous solids. It is interesting that the simultaneous absorption decrease at 485 nm and at around 700 nm in the thermal reaction is similar to the results obtained in the photoreaction at 25 K for SNO/PS [11], where the absorption at 485 nm is interpreted as another electronic transition of the species absorbing at 700 nm.

The fact that the integrated area of ΔOD spectra is approximately conserved in the early times and then slowly decreases with time is shown in Fig. 3(B). The reaction of X to SNO causes the decrease in the integrated absorption intensity in the visible region, while the thermal reaction of X to PMC results in a slight change in the absorption spectra. Therefore, it is clear that at 25 K the former reaction is slower than the latter.

From the above discussions, one general point becomes very clear: X experiences thermal transformation to yield at least three different types of PMC isomers, $PMC_{530}$, $PMC_{570}$, and $PMC_{605}$. And these results directly indicate that X is the reaction intermediate trapped at a low tempe-

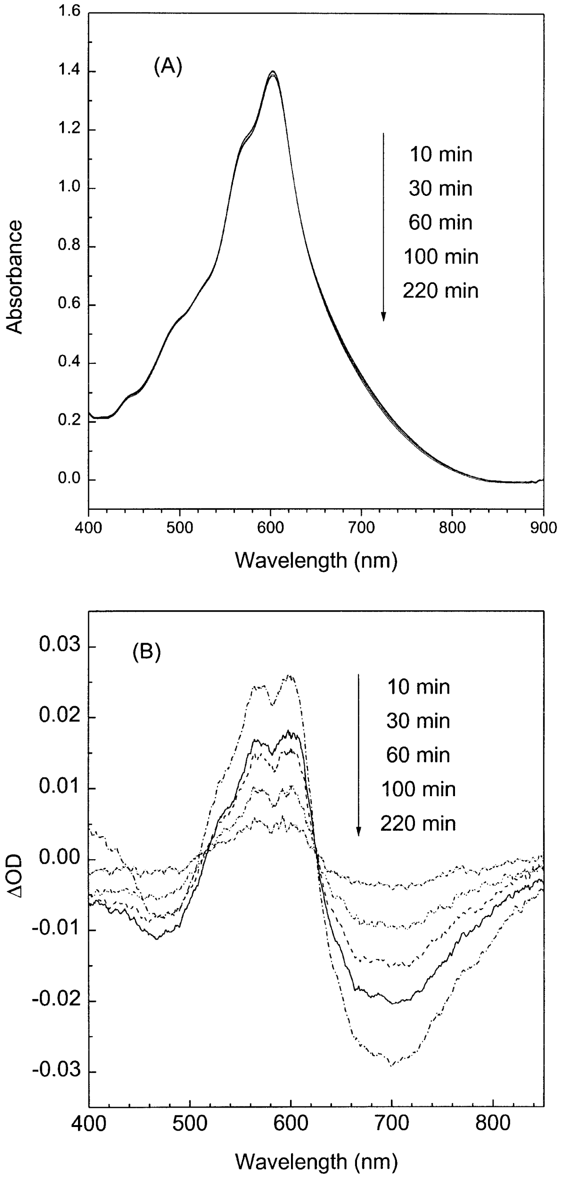

Fig. 3. Absorption (A) and ΔOD spectra (B) of PMC/PS at 25 K in the dark as a function of elapsed time after UV irradiation.

rature during the SNO to PMC photoconversion. Because not only the increase in the absorbance but also the absolute absorbance at 570 nm is larger than those values at 530 nm, it seems that $PMC_{570}$ is thermodynamically more stable than $PMC_{530}$. However, it is ambiguous whether $PMC_{570}$ is relatively more stable than $PMC_{605}$ because of the interplay between the decrease of X and the increase of $PMC_{605}$.

The thermal reactions of SNO/PS at 77 K are illustrated in Fig. 4. The ΔOD spectra at 77 K consist of several characteristic structures superimposed on the top of the broad hole (absorption decrease). This result indicates that the principal reaction at 77 K is the PMC → SNO reaction. Because of the higher thermal energy and because of the smaller amount of X at 77 K than those at 25 K, the thermal PMC → SNO reaction becomes significant and, therefore, the decrease in absorption is obtained throughout the absorption band. Meantime, the thermal X → PMC reaction is also in progress although the amount of X trapped is small. This reaction causes both the absorption decrease at 485 nm and at around 630–700 nm and the absorption increases at around 605, 570 and 530 nm. If the relative amount and the width of the site distribution of each PMC isomers produced by the photochemical SNO → PMC reaction are same as those produced by the thermal X → PMC reaction, then the ΔOD spectra will be just the sum of decrease in the absorption of PMC and X. However, because the reactions take place in the polymer at temperature below $T_g$, the assumption that the width of the site distribution of PMC produced by thermal reaction will be narrower seems to be plausible. Thus the interference between the thermal PMC → SNO reaction and thermal X → PMC reaction seems to result in the complexity in the ΔOD spectra. The upward structures, indicated by the asterisks are located at 530, 570 and 610 nm, appear to be due to the production of PMC isomers from X. Although the experiments are performed in the same condition, slightly different amount of X are trapped in the polymer matrix due to the inherent disorder of the matrix and, therefore, the ΔOD spectra slightly vary case by case.

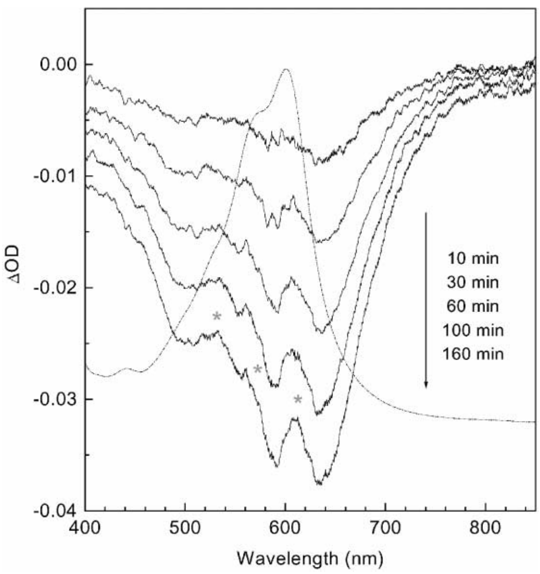

Fig. 4. ΔOD spectra of PMC/PS at 77 K in the dark as a function of elapsed time after UV irradiation.

From the Figs. 1–4, it is clear that ΔOD spectra are greatly affected by the temperature because of the thermal energy and because of the amount of X trapped in the polymer. This also indicates that the thermal PMC → SNO reaction is the principal reaction at 150 K, while the thermal X → PMC reaction is the representative reaction at 25 K.

From these discussions, the potential energy surface along the reaction path in the ground electronic state, which is proposed in Ref. [19], can be better described. Because the toluene is similar to the repeating unit of PS, it is assumed that in PS the enthalpy change for the thermal

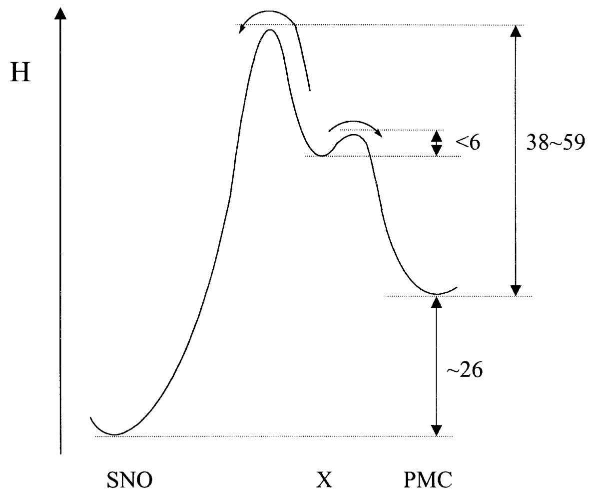

Fig. 5. Potential energy surface along the reaction path of SNO/PS in the ground electronic state.

SNO → PMC reaction is similar to that measured in the toluene, 26.4 kJ/mol [17]. The activation energy for the thermal PMC → SNO reaction in PS is known to depend on the aging time, i.e., it is 55 kJ/mol at around room temperature for the sample made 10 days prior to the measurements, while it is 40 kJ/mol for the sample made 38 days prior to the measurements [18]. By considering the aging time, the activation energy for the thermal PMC → SNO reaction in PS is not much different from that in toluene [19]. On the other hand, the activation enthalpy for the thermal X → PMC reaction at 25 K is roughly estimated as $<6$ kJ/mol. The energy difference between X and $\mathrm{PMC}_{605}$ varies in a wide range and is roughly estimated as $\sim 27$ kJ/mol in average based on the assumption that potential energy surface in the excited electronic state is flat. Combining these values, we propose Fig. 5 as the primitive potential energy surface in the ground electronic state. It shows that the intermediate X is located in average at about the middle between PMC and the transition state. The fact that the activation energy for the reaction X → PMC is lower than that of X to SNO implies that the former reaction is faster than the later one.

In summary, the thermal behaviors of non-planar photoproduct X and PMC form of SNO dispersed in PS have been studied by a low-temperature UV/Vis absorption spectroscopy. It shows that the ΔOD spectra are greatly influenced by the temperature due to the different thermal energy. Although the reaction rates are extremely slow at 25 K, X experiences not only the thermal bleaching reaction to SNO but also the thermal transformation to yield at least three different PMC isomers. At higher temperatures, the thermal bleaching reaction from PMC to SNO prevails over the thermal reactions of X to PMC resulting in the absorption decrease in the visible region. The experimental results are utilized to describe better the potential energy surface along the reaction path in the ground electronic state.

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