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A low temperature spectrophotometric study of the photomerocyanine form of spirooxazine doped in polystyrene film

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Abstract

The photocoloration and photobleaching reactions of spironaphthooxazine doped in polystyrene have been studied by using low-temperature absorption spectroscopy. The absorption spectra of PMC produced at 25 K are remarkably different from those obtained at 77–200 K with regard to the broad absorption gains at around 670 and 485 nm. Upon visible irradiation, PMC undergoes photobleaching reaction whose efficiency varies with the irradiation time and wavelengths. Regardless of the irradiation wavelength, the broad holes were initially produced at 25 K on both sides of the absorption spectra while the antihole is obtained at around 530–600 nm. As time passes, the centroid of the hole gradually shifts toward the burn wavelength. From experimental observation, the broad absorption located at around 485 and 670 nm are attributed to the nonplanar photoproduct X trapped in the polymer matrix. Therefore the hole and antihole observed at the very early stage of the visible irradiation are interpreted as being due to the photochemical transformation of X to transoids. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Spirocompounds have been intensively investigated over many years because of scientific interest and their potential for practical applications such as display systems, optical switching and optical memory storage systems [1–6]. However, most of these researches concentrate on their synthesis and applications. Concerning the mechanism of isomerization and photophysical and photochemical properties of the spirocompounds, little is known.

Spirooxazines (SO) are of particular interest among spirocompounds due to their relatively high photostability [1,7,8]. Upon UV irradiation, colorless SO experience a reversible photochemical transformation to their colored photomerocyanine form (PMC) [1]. This involves heterolytic cleavage of the C–O spirobond of the oxazine ring followed by a rotation of the two parts of the molecule in relation to each other so as to achieve coplanarity (Scheme 1). Then the open form PMC tends to revert back to SO either thermally or photochemically.

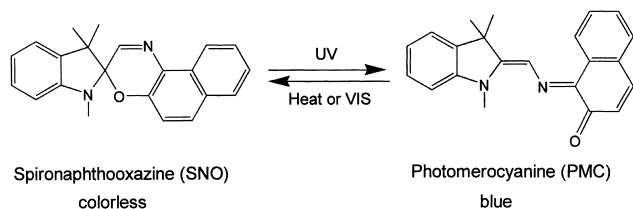
It is well known that the absorption and fluorescence spectra for PMC of spiropyran (SP) change dramatically

depending on the UV irradiation temperature due to the presence of different kinds of isomers of PMC [3,6,9], each of which has its characteristic absorption spectrum. However, the absorption spectra of PMC for SO are known to be temperature independent over a wide temperature range 77–300 K regardless of both in solvent polarity and polymer matrices [7,10,11]. When SO doped in amorphous solids are illuminated with visible light at extremely low temperatures, however, there is a possibility that the absorption spectra are quite different from those obtained at 77–300 K due to the low thermal energy and the structural disorder of the matrix. This process appears fairly plausible as long as the energy required for cleavage of the C–O bond and for rotation of the two parts of the molecule is supplied either in the form of radiation energy or thermal energy.

In this study, attention is directed at obtaining a better understanding of the photochemical SO to PMC conversion. We present UV–Vis spectroscopic results obtained at low temperatures on 1,3-dihydro-1,3,3-trimethyl-spiro[2H-indol-2,3'-[3H]naphth[2,1-b][1,4]oxazine] (spironaphthooxazine, SNO). Using the photobleaching experiment, we present, for the first time, the evidence of the presence of the primary photoproduct of SNO in the steady-state absorption spectra.

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Scheme 1.

2. Experimental

2.1. Materials

SNO was purchased from Tokyo Kasei Kogyo and used without further purification. Polystyrene (PS) and spectrograde solvents were purchased from Aldrich. The SNO solution was prepared in various solvents at concentrations ranging from 8.0×10^{-3} M \sim 2.0×10^{-2} M. Thin polymer films containing 5 wt.% of SNO were prepared from toluene by the solvent-cast method. Sections of films were cut from the dried film and mounted in a variable temperature cryostat (Janis, RGC-210).

2.2. Spectroscopic study

Absorption spectra of the sample were recorded at desired temperatures using a UV/VIS spectrophotometer (Shimadzu 2100S) which is interfaced to an IBM compatible-PC. Photocoloration of SNO doped in PS (SNO/PS) was achieved with 337 nm laser pulses from an N₂ laser (Laser photonics LN-1000) at desired low temperatures. In order to control the temperature of the sample, it was placed in the cryostat controlling the temperature to within ± 0.1 K (Lakeshore Model 330 temperature controller). Before the measurements of the absorption spectra or the photocoloration experiment were made, the sample was kept at the desired temperature for at least 30 min. The photobleaching experiments were performed using two He-Ne lasers (a Laser research 5 mW and a Uniphase 1677) and a laser diode (Opti 4). The photoirradiation time was controlled with a mechanical shutter (Uniblitz T132).

3. Results and discussion

Upon UV irradiation or by heating, colorless SNO are transformed into the colored PMC form that reverts back to the colorless SNO in the dark or by visible irradiation. The rate of the thermal back reaction depends to a great extent on the temperature of the sample. The thermal back reaction slows down as the temperature decreases and finally stops at around -60°C [1]. In this study, the photobleaching reaction of PMC has been studied at 25 K in order to eliminate interference by the thermal back reaction.

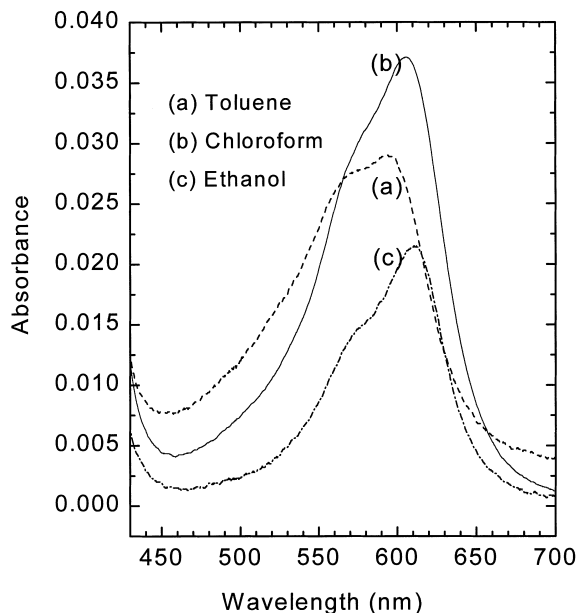


Fig. 1. The absorption spectra of PMC of SNO in various solvents at 25°C : (a) 2.0×10^{-2} M in toluene; (b) 8.0×10^{-3} M in chloroform, and (c) 2.0×10^{-2} M in ethanol, respectively.

3.1. Absorption spectra in various environments

Fig. 1 represents the absorption spectra of SNO recorded at 25°C using the scanning double-beam spectrophotometer. The concentration of the sample is 8.0×10^{-3} M for chloroform and 2.0×10^{-2} M for toluene and ethanol solution. The absorption spectra of PMC in liquid solutions were obtained through thermochromic reaction. It is clear that the shapes and positions of the absorption band depend to a great extent on the polarity of the environments. The most prominent absorption band in ethanol solution is located at 612 nm and shoulder at 578 nm. However, the intensities of the corresponding two bands are about the same in toluene solution; for chloroform solution it is halfway between the two. These observations qualitatively agree with those of Refs. [12,13]. Based on the similarity between SNO and SP [14,15], the shoulder at 578 nm is thought of not as a vibronic band but as an origin band of one isomer, which is different from the one responsible for the band at 612 nm. According to Fig. 1, it is clear that the amount of the isomer responsible for each band changes depending on the solvent polarity and medium viscosity. Because the relative absorption in the 612 nm region is larger in polar solvent, it seems that the 612 nm absorbing species probably has a larger dipole moment than the 578 nm absorbing species does. However, it is noteworthy that the absorption spectra of PMC in toluene has a longer tail on the red side and a broad band on the blue side as compared with those in ethanol and chloroform. For spiro naphthopyran, whose structure is very similar to that of SNO, the temperature and solvent effects on the absorption spectra are interpreted in terms of the presence of the stereo isomers [6]. However, because the formation of the photoinduced aggregation in nonpolar solvent is sometimes

reported for SP containing a nitro group [16], the possibility of the aggregate formation of PMC for SNO in toluene cannot be completely excluded.

3.2. Absorption spectra of PMC at low temperatures

It is well known that the absorption spectra of PMC of the SP derivatives depend on the irradiation temperature [3,6,9] while those of SNO derivatives are temperature independent over a wide temperature range [7,10,11]. Therefore, it is generally thought that the temperature independence of the absorption spectra of PMC of SNO is a common property for all photoinduced SNO. However, our experimental data show that the situation is quite different when SNO dispersed in amorphous solids is irradiated with UV at 25 K.

Fig. 2 shows the absorption spectra of PMC form doped in polystyrene. UV irradiation and spectral measurement were performed at the same temperatures indicated in the figure. It shows that the absorption spectra of the colored modifications of SNO/PS, which have absorption maximum located at 605 nm and shoulder at 570 nm (and probably at 530 nm), are almost independent of the UV irradiation temperature over a wide temperature range 77–200 K. This result agrees with the previously published experimental results [7,10,11].

However, the absorption spectrum measured at 25 K is remarkably different from those measured at higher temperatures. Similar results were obtained for SNO doped in polymethylmethacrylate (not shown). The most prominent characteristic is the presence of the broad absorption tail on the red side and a weak shoulder on the blue side of the

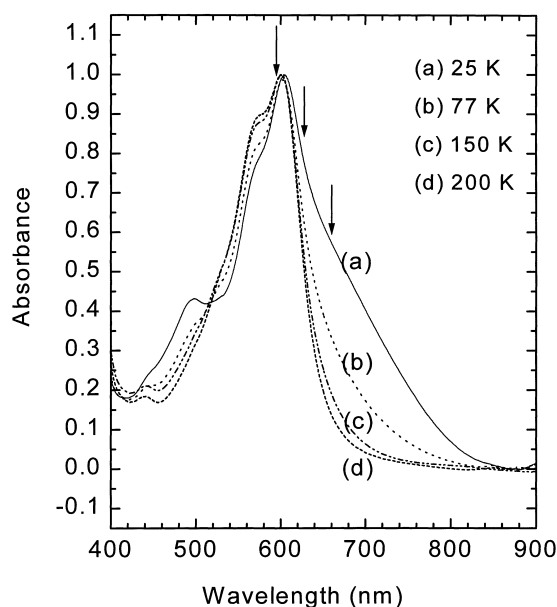


Fig. 2. Normalized absorption spectra of PMC doped in polystyrene film. UV irradiation was performed with 337 nm pulses from the N_2 laser at the temperatures indicated in the figure. The absorption spectra were measured at the same temperatures. The arrows indicate the wavelength of the visible light used in the photobleaching experiment.

absorption band whose intensities slightly vary case by case. The high-energy side shoulder is located at around 485 nm and the low-energy side tail extends up to around 900 nm. In particular, compared to those obtained at higher temperatures, widespread substantial absorption gain in the low energy side tail is distinctive. It is unlikely that a variation of 52 K in temperature causes the dramatic change on the absorption spectra for the same species. Instead, we interpret the relatively large absorption at these two positions as being due to the presence of new species of PMC, which scarcely exist at 77–200 K but may exist at very high temperatures by the thermal equilibrium. The large increase in absorption can be attributed to the substantial production of new species and the widespread distribution in absorbance seems to be due to the large disorder of the matrix. The isomer is analyzed in detail later.

3.3. Photobleaching reaction

To characterize the chemical species responsible for the absorption in both sides of the absorption spectra, photobleaching experiments on PMC/PS, which is produced at 25 K, are performed at 25 K. Fig. 3(A) represents the absorption spectra of PMC as a function of the irradiation time. The photoirradiation on PMC was achieved with a 594 nm cw laser and light intensity was controlled using neutral density filters. The fact that the photobleaching reaction with visible light is still operative at an extremely low temperature, such as 25 K, indicates that the activation barrier at the excited state potential energy surface along the reaction path is very small or negligible. Because the total absorption intensity is decreased, it is suggested that most of PMC is transformed into SNO. At prolonged photoirradiation times, the shapes of the absorption spectra are different from the pre-burn spectrum due to the different photobleaching efficiency at different wavelengths. This also indicates the presence of several different species.

Fig. 3(B) represents ΔOD spectra (the post-burn minus pre-burn spectrum) of Fig. 3(A). It clearly shows that ΔOD spectra are greatly influenced by the irradiation time. At the very early stage of the photoirradiation, absorbances both at a shoulder around 485 nm (PMC_{485}) and the red side tail are decreased although absorbances at these positions are relatively low and the burn wavelength (λ_B) 594 nm is far from both 485 and 670 nm. The absorption decrease will be called a “hole”. As the irradiation time gets longer, the hole located at 605 nm, which corresponds to the absorption maximum of PMC, gradually grows and becomes comparable to the hole at 640 nm.

The results of the photobleaching experiment with λ_B of 632.8 and 660 nm are shown in Figs. 4 and 5, respectively. The photoirradiation and spectral measurements are performed at 25 K. Comparison of Figs. 4 and 5 with Fig. 3 shows the dependence of ΔOD spectra on λ_B . As λ_B changes from 594 to 660 nm, the hole at 605 nm in the ΔOD spectra gets smaller. The hole centered at 485 nm is relatively

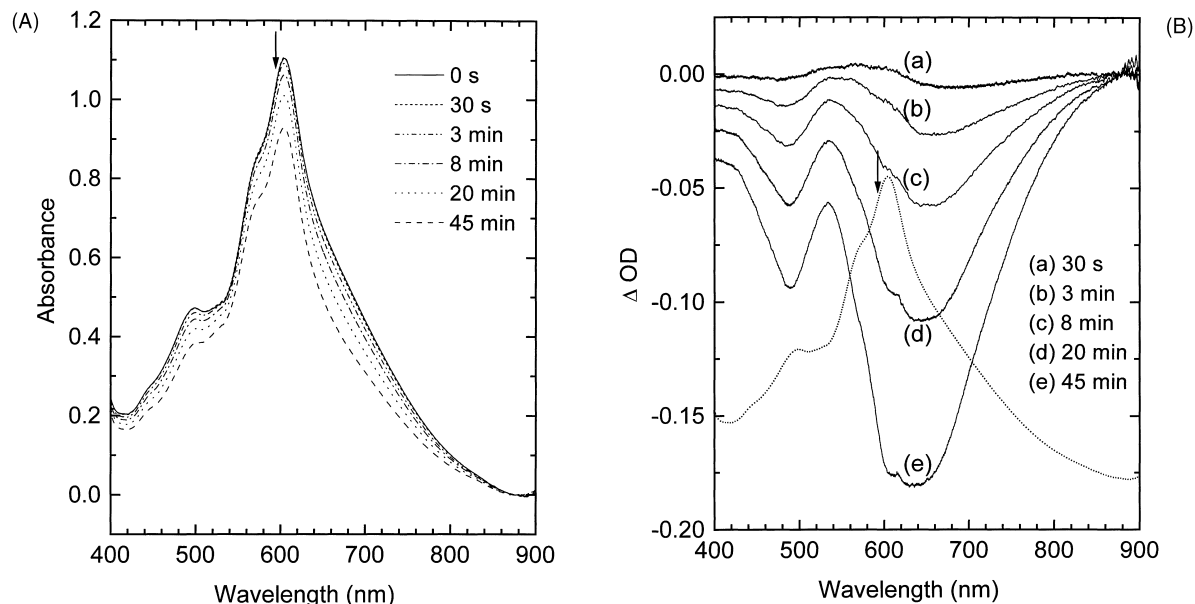


Fig. 3. The absorption and ΔOD spectra of PMC/PS as a function of burn time. The arrow indicates the burn wavelength, 594 nm. The temperature was 25 K and the burn power was $10 \mu\text{W}$: (A) absorption spectra, and (B) ΔOD spectra.

narrow and continuously grows with the irradiation. Its relative depth was approximately 45% of hole maximum during the irradiation and seemed almost independent of λ_B . At the beginning of the photobleaching, the centroids of hole spectra are located near 670 and 485 nm regardless of λ_B . We will refer to the species responsible for absorption at these positions as PMC_{670} and PMC_{485} . As the irradiation time gets longer, however, the centroid of the hole slowly shifts toward the burn wavelength. This indicates PMC_{670} is burned faster than PMC_{605} , and therefore its hole depth is deeper at the early stage of the burning. Thus the relative

amount of PMC_{670} to PMC_{605} is decreased at longer burn times, and therefore, the burning from PMC_{605} becomes relatively important. The dependence of the shape of ΔOD spectra on the burn time and λ_B also supports the presence of the different isomers.

Contrary to the absorption decrease on the both sides of the absorption spectra, the slight absorption increase at around 550 nm is observed regardless of λ_B at the initial photobleaching stage. Its position is closer to λ_B than the shoulder at 485 nm and its absorbance is comparable to those at 485 and 670 nm. The antihole (absorption increase)

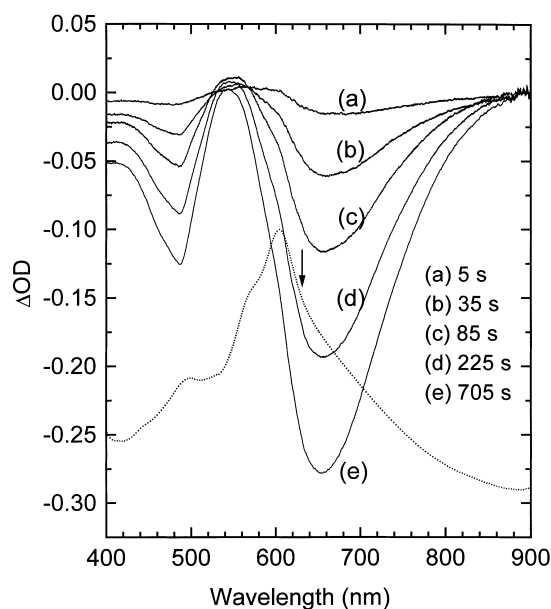


Fig. 4. The ΔOD spectra of PMC/PS at 25 K as a function of burn time. The arrow indicates the burn wavelength, 632.8 nm. The burn power was $50 \mu\text{W}$.

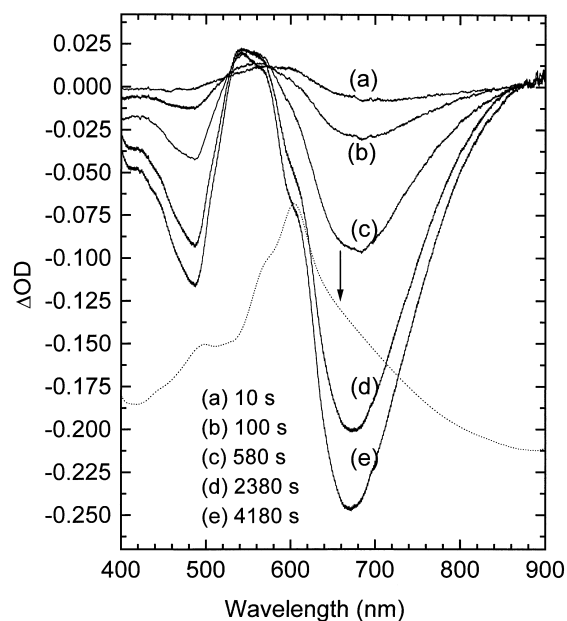


Fig. 5. The ΔOD spectra of PMC/PS at 25 K as a function of burn time. The arrow indicates the burn wavelength, 660 nm. The burn power was $40 \mu\text{W}$.

seems to consist of three peaks centered at 605, 570 and 530 nm, which are almost coincident with the peak position of the absorption spectra. We will denote them as PMC_{605} , PMC_{570} and PMC_{530} , respectively. Because UV light is completely blocked during the photobleaching experiment, the antihole is not likely to be produced directly from SNO. Based on the simultaneous production of the hole and antihole, it is rather supposed to have its origin in the photochemical transformation of PMC_{485} and PMC_{670} into PMC_{605} , PMC_{570} , and PMC_{530} . Since there is almost no potential barrier in the excited state, the PMC would be excited to its first excited state with visible irradiation, and then moves toward the position where the reaction occurs. By comparing the relative intensities of the hole and antihole, it is deduced that PMC_{670} and PMC_{485} is mainly converted into SNO leaving holes in both regions while only a small fraction experience a photo-conversion into PMC_{530} , PMC_{570} , or PMC_{605} to give rise to the production of the antihole.

The antihole shape depends on the λ_B and burn time. As the burn wavelength changes from 594 to 660 nm, the antihole becomes more prominent. When burned with 594 nm, antiholes completely disappear within 3 min. When λ_B is equal to 660 nm, the antihole at 605 nm disappears within 4 min leaving only a small glitch in the sharply falling edge while the antihole at 530 nm still exists after prolonged irradiation (longer than 1 h). Generally the antihole at 605 nm disappears more rapidly than the other two. As mentioned earlier, the centroid of the hole slowly shifts from 670 nm to λ_B with burn time, and the antihole production is relatively small compared with the hole production. Therefore, the dependence of the antihole shape on λ_B and the presence of the glitch are a consequence of the interplay between the negative-going broad hole and positive-going antihole. These observations indicate the presence of at least three PMC isomers, which are probably all trans with respect to the central C=N bond without having any appreciable steric hindrance. The presence of three species is more clearly observed from the thermal reaction of PMC_{485} and PMC_{670} at 25 K [17].

3.4. Nonplanar PMC photoproduct

The broad tail on the red side and the shoulder on the blue side of the absorption spectra at 25 K represented in Fig. 2 may have their origin in the existence of the new species, either in the form of the aggregate or nonplanar photoproduct. In the formation of H- and J-aggregates of PMC, it is not easy to explain how the significant amount of aggregation occurs in the rigid polymer matrix. One possible explanation is that the close packing of PMC necessary for aggregate formation is provided by possible aggregation of SNO during the solvent evaporation after casting of the films. Because the aggregates are equilibrium species of PMC and stabilized in the low temperatures, these should be observed when SNO is irradiated with UV light at 150 K and

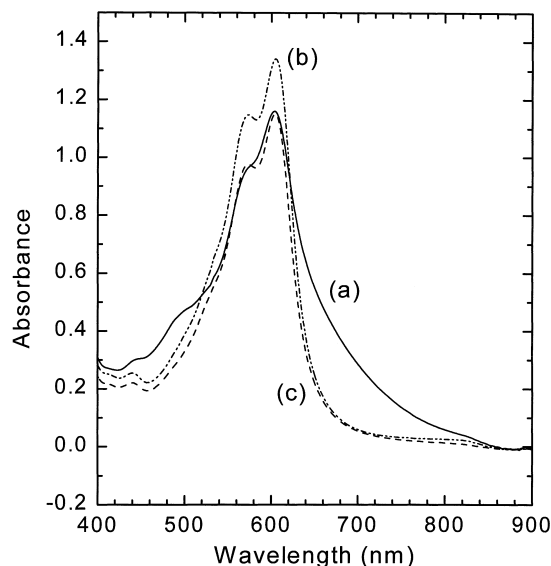


Fig. 6. Absorption spectra of PMC doped in polystyrene film. UV irradiation was performed with 337 nm pulses from the N_2 laser: (a) after UV irradiation at 25 K, (b) after UV irradiation at 25 K followed by heating to 150 K and then recoiling to 25 K, (c) after UV irradiation at 150 K followed by cooling to 25 K.

subsequently cooled down to 25 K. However, as shown in Fig. 6, the spectrum of PMC obtained in that way is not similar to that of PMC produced by UV irradiation at 25 K and measured at 25 K but rather closely similar to that of PMC produced and measured at 150 K. Furthermore, the broad tail on the red side and the shoulder on the blue side of the absorption spectra of PMC produced and measured at 25 K are not restored when it experiences the thermal cycling, heating to 150 K and recoiling to 25 K. These observations indicate that the nonequilibrium forms of the PMC are created by UV irradiation in the rigid polymer matrix at 25 K. In the formation of the nonequilibrium species, the properties of the polymer matrix should be accounted for. Under the glass transition temperature T_g , the amorphous solid is not in thermal equilibrium due to the low thermal energy, and therefore, has its inherent structural disorder [18]. Since the guest molecules doped in the amorphous solid are coupled with the matrix, the properties of the guest molecules probably depend on the local potential energy and the local free volume of the matrix. Particularly at extremely low temperatures, the molecular motion of the guest molecule may be frozen due to the low thermal energy.

When the SNO/PS is irradiated with UV light at extremely low temperatures, such as 25 K, the rotation of the two parts of the molecule, which is preceded by the C–O cleavage, may be limited depending on the local potential energy it is coupled with. Therefore, various types of conformational isomers having torsional angle θ between 0° and 180° about the central partial C=N double bond may be trapped in the matrix. Probably the majority of the isomers trapped could be the relatively stable transoids ($\theta \sim 180^\circ$),

which may appear as PMC₆₀₅, PMC₅₇₀ or PMC₅₃₀ at the higher temperatures studied (77–200 K), while cisoids ($\theta \sim 0^\circ$) may not be stabilized due to their high steric hindrance. Meanwhile, the absorption on the both sides of the absorption spectra are thought to be due to the nonequilibrium species. One good candidate for the nonequilibrium species is the photoproduct (X) having intermediate torsional angles or having a structure similar to SNO but with a cleaved C–O spirobond. Because at 25 K the thermal energy is too low for the system to have kinetic access to lower potential minima in a rigid medium, the spontaneous conversion of the unstable nonplanar intermediate X into the other isomer is strictly limited. Since X will absorb different frequency of light, the absorption spectrum at 25 K will be different from those obtained at the higher temperatures studied. This is clearly shown in Fig. 2. Therefore, we attribute the additional absorption on both sides of the absorption spectra to the substantial production of X. The fact that the absorption spectra at 25 K are different from that at 77 K indicates that most of X trapped at 25 K in very shallow potential wells may have kinetic access at 77 K to lower minima by going over the potential barrier and finally giving rise to more stable isomer transoids. The fact that the tail on the low energy side of the absorption band is very broad, seems to indicate the formation of the various intermediates.

The absorption band at 485 nm could originate from the vibronic transition or another electronic transition of the 670 nm absorbing species. Or it may be the origin band of the comparable isomer, which is different from PMC₆₇₀. The absorption at around 485 nm is depleted even by 660 nm light which is more than 5000 cm^{-1} away from the 485 nm and the hole depth at 485 nm continuously grows with the maximum of the hole around 660 nm region by keeping the relative intensity of 45%. Therefore, it is more plausible to attribute the absorption around 485 nm to the another electronic transition of PMC₆₇₀. It is very interesting to compare our experimental results with those of the time-resolved data obtained for SNO and SP. Although the different groups have slightly different results, and therefore, different interpretations, many groups have observed transient absorption at around 400–500 nm and/or 550–700 nm [19–24]. Especially, Chibisov et al. [19,20] observed the transient absorption of 6-nitro-SP in acetone at around 410 and 640 nm and ascribed this to one of the possible rotamers with *cis* isomer structure. It is very surprising that their transient absorption spectra are very similar to our ΔOD spectra initially obtained in the visible irradiation. In order to obtain a better understanding of the photochemical SNO to PMC conversion, temperature dependent photobleaching experiments are in progress.

In conclusion, the photocoloration and photobleaching reactions of SNO/PS system have been studied by using low-temperature absorption spectroscopy. The absorption spectrum of PMC produced at 25 K is very different from those obtained at 77–200 K as there are broad absorption increase

at around 485 and 620–900 nm. Depending on the visible irradiation time and wavelengths, PMC undergoes photobleaching reaction with different efficiency. At the very early stage of the photoirradiation at 25 K, the absorption on the both sides are initially depleted while the antihole is produced in the 530–600 nm region regardless of the burn wavelength. As time passes, the centroid of the hole gradually shifts toward the burn wavelength. From the experimental observation, the broad tails at around 485 and 670 nm observed at 25 K are attributed to the nonplanar photoproduct X trapped in the polymer matrix. Therefore the hole and antihole observed at the early stage of the visible irradiation are interpreted as being due to the photochemical transformation of X to transoids.

Acknowledgements

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