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PHOTOCHROMIC REACTIONS OF 4-[BIS(9,9-DIMETHYLFLUOREN-2-YL)AMINO]AZOBENZENE IN LOW MOLECULAR-MASS ORGANOGELS

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ABSTRACT

In order to gain information about the environment at the solution region within the low molecular-mass organogels, photochromic reactions of title compound were investigated in 12-hydroxystearic acid– and 1,2-(1S,2S)-bis(stearoylamino)cyclohexane–toluene gels in comparison with those in toluene solution. The results suggested that the environment at the solution region within these gels was essentially the same as that in toluene solution although a small fraction of gelator molecules did not embedded in the gel network but existed in the solution region.

Keywords Low molecular-mass organogel, Azobenzene, Photochromism, Photostationary state, Quantum yield, Rate constant

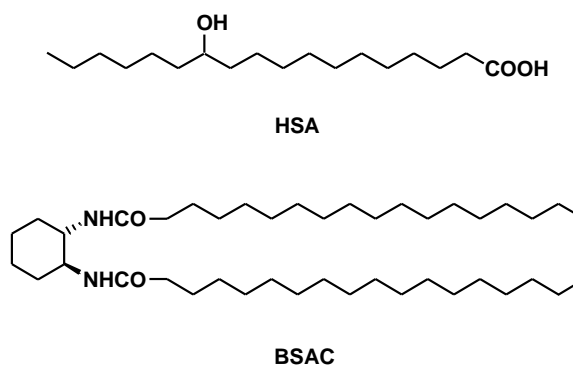
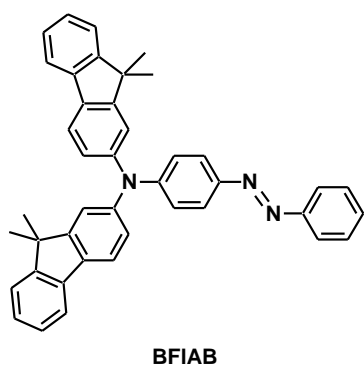
INTRODUCTION

Gel composed of low molecular-mass organic gelators with organic solvents, namely

"low molecular-mass organogel", is a unique form as one of the soft materials. It is believed that the three dimensional network is constructed by aggregation of gelator molecules and organic solvents are held in the network. Intermolecular interactions between gelator molecules such as hydrogen bonds are believed to play an important role for the aggregation of the gelator molecules to form fibers which construct such three dimensional network. A variety of gelators have been developed and their structures and properties have been investigated (1–9). With regard to a typical low molecular-mass organogel based on 12-hydroxysebacic acid (HSA), it has been shown that the gelator molecules aggregate to form fibers in the organogels, in which zigzag sequences of intermolecular hydrogen bonding are produced along the fiber axis (2). Rheological properties and structural correlation in the organogels have been investigated in detailed (4). In contrast to the dense colloidal polystyrene hydrogels which was shown to be fractal gels (10,11), small angle neutron scattering (SANS) study of HSA organogels have demonstrated that the HSA organogel did not indicate the results expected for a fractal structure (4). In addition to such fundamental studies, introduction of photochemical and photophysical functions to the gelator is also the subjects of interest (7,12–18).

A lot of studies regarding low molecular-mass organogels, however, seem to have just addressed their structures of the three dimensional network and their properties related to the formation of the network, and not so much attention has been paid to the solution region held in the network. Since the environment at the solution region within the gels might be affected by the network, it is of interest and of importance to elucidate the environment at the solution region comparing with that in the usual solution. It has been reported that the photochromic reaction of azobenzene derivatives in polymer matrices and low molecular-mass amorphous films provide information about their local environments (19–23). Thus the photochromic reaction of an azobenzene derivative existing in the organogel might

provide information about the environment in the organogel. We have reported the synthesis of 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFIAB) and its analogues and their photochromic reactions as amorphous films, which indicated that the reactions were affected by the environment (23). Thus in the present study, we have selected the photochromic reactions of BFIAB as a probe for gaining information about the environment at the solution region within low-molecular mass organogels. With regard to low molecular-mass gelators, we chose HSA and 1,2-(1S,2S)-bis(stearoylamino)cyclohexane (BSAC) (7), that provide clear gels with toluene, being preferable for optical measurements. Phase diagrams for HSA–organic solvents systems have been elucidated, showing that the gel-sol transition temperature of HSA–toluene system with the HSA concentrations of 1-10 wt% was ca. 40 °C (24). With regard to BSAC, phase diagrams of BSAC with a variety of solvents were elucidated, showing gel-sol transition temperature of ca. 75 °C for BSAC–decalin system with BSAC concentrations of 0.01-0.06 M⁻¹ (7). Thus, the photochromic properties of BFIAB in HSA– and BSAC–toluene gels were investigated in comparison with those in toluene solution in the present study.



EXPERIMENTAL

Materials

BFIAB (23) and BSAC (7) were prepared by the previously reported procedures. HSA

was purchased commercially (Tokyo Chemical Industry Co., Ltd.) and used without further purification.

Sample preparation

For measurement of electronic absorption spectra of the gel, appropriate amount of HSA or BSAC was dissolved in toluene solution of BFIAB by heating at ca. 70 °C. The resulting solution was added into the sample cell (optical path length: 1 mm) and then cooled with ice/water to give transparent gels.

Measurement and apparatus

Photoisomerization of BFIAB in toluene solution and in the gels was carried out by irradiation with 450 nm-light with a bandwidth of 10 nm from a 500 W Xenon lamp (UXL-500D, USHIO) through an interference filter (IF-S 450, Vacuum Optics Co.) using an optical fiber. Photochromic reactions were analyzed from the change in the electronic absorption spectra measured with a Hitachi U-3500 spectrophotometer. The sample was kept at a constant temperature (30 °C) by using a temperature controller (SPR-10, Hitachi, Ltd.).

RESULTS AND DISCUSSION

Before investigation of photochromic reactions of BFIAB in the gels, we checked the gelating ability of HSA and BSAC. It was confirmed that more than ca. 20 mg of HSA was needed for gelation of 1 mL toluene while only a few milligrams of BSAC was needed. The resulting gels were found to be clear and were confirmed that the scattering of the light with a wavelength at around 450 nm was small (the transmittance was larger than 98%) enough to investigate the photochromic reactions of BFIAB in these gels.

At first, electronic absorption spectra of BFIAB in the HSA–toluene (HSA: 50 mg mL⁻¹)

and BSAC–toluene gels (BSAC: 5 mg mL⁻¹) were compared with that in toluene solution in the dark. The spectrum in BSAC–toluene gel was almost identical to that in toluene solution (Fig. 1a). The feature of the spectrum in the HSA–toluene gel was also the same as that toluene solution; however, the absorbance was found to be ca. 4-5 % smaller than that in toluene solution (Fig. 1b). When the amount of the HSA decreased to 30 mg mL⁻¹, the reduction in absorbance became smaller (ca. 2-3 %). These results suggested that the gel network displaced the solution to the periphery, resulting in a decrease of the actual optical path length through the solution region in the experimental optical cell. Consequently, it is suggested that BFIAB molecules did not embedded in the three dimensional network but existed in the solution region, and hence the photochromic reactions of BFIAB in the gels described below were expected to provide information about the environment at solution region within the gels. With regard to the BSAC–toluene gel, relatively small amount of BSAC molecules (5 mg mL⁻¹) existed in the BSAC–toluene gel as described above, so that the difference in spectrum between for the gel and for the solution could not be detected.

BFIAB was found to exhibit photochromism in HSA– and BSAC–toluene gels as well as in solution. Upon irradiation of HSA–toluene gel (HSA: 50 mg mL⁻¹) including BFIAB, the absorbance of the band at around 450 nm gradually decreased due to the trans–cis photoisomerization, and the reaction system finally reached the photostationary state (Fig. 1c). When irradiation was stopped after the reaction system had reached the photostationary state, the electronic absorption spectrum gradually recovered to the original one due to the backward cis–trans thermal isomerization. Similar spectral changes were observed for the BSAC–toluene gel including BFIAB.

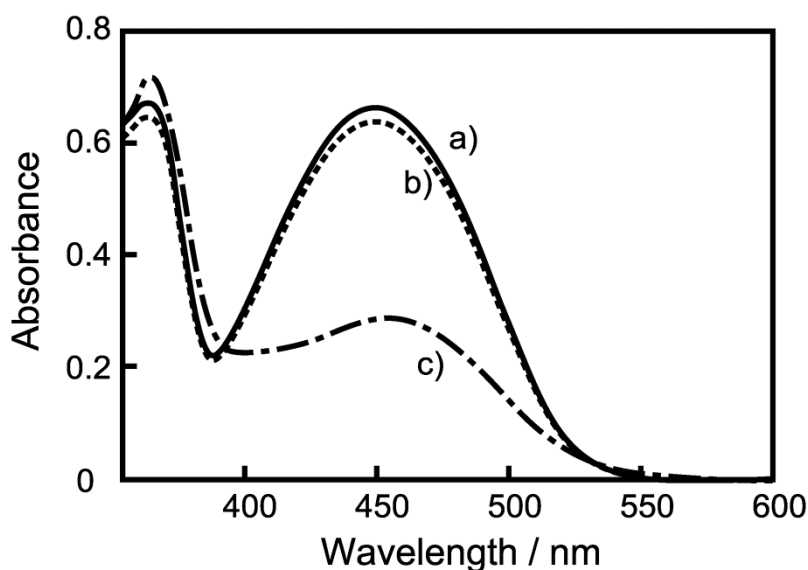


FIGURE 1 Electronic absorption spectra of BFIAB. a) toluene solution in the dark. b) HSA–toluene gel (HSA: 50 mg mL⁻¹) in the dark. c) HSA–toluene gel (HSA: 50 mg mL⁻¹) at photostationary state upon irradiation with 450-nm light. [BFIAB] = 2.7 × 10⁻³ mol dm⁻³.

The fraction of the photogenerated cis-isomer at the photostationary state (Y_{pss}) was determined experimentally from the following Eq. (1);

$$Y_{\text{pss}} = [1 - (A_{\text{pss}}/A_{\text{trans}})] / [1 - (\epsilon_{\text{c}}/\epsilon_{\text{t}})] \quad (1)$$

where ϵ_{t} and ϵ_{c} represent the molar extinction coefficients of the trans- and cis-isomers at a measured wavelength, A_{trans} and A_{pss} the absorbance of the sample at the same wavelength before photoirradiation and at the photostationary state, respectively. Assuming that both values ϵ_{trans} and ϵ_{cis} in the gel were equal to those in toluene solution (23), the Y_{pss} values for the HSA– and BSAC–toluene gels upon irradiation with 450 nm-light were estimated to be 0.74, being the same as that in solution (Table 1).

When the concentration of cis-isomer is small enough to neglect the contribution of the cis–trans isomerization reactions, the decay of trans-isomers upon photoirradiation at initial

stage can be written as Eq. (2) (23);

$$-\ln ([trans]_t/[trans]_0) = [10^3 I_0 (1-10^{-A_{trans}})/A_{trans}] \epsilon_t \Phi_t t \quad (2)$$

where $[trans]_0$ and $[trans]_t$ are the concentrations of trans-isomer before photoirradiation and at irradiation time t , I_0 the intensity of incident light [$\text{einstein cm}^{-2}\text{s}^{-1}$], and Φ_t the quantum yield for the trans–cis photoisomerizations. Here, values of $[trans]_t/[trans]_0$ were experimentally determined by absorbance change of the as $[(A_t/A_{trans})-(\epsilon_c/\epsilon_t)] / [1-(\epsilon_c/\epsilon_t)]$, where A_t it the absorbance at irradiation time t . As shown in Fig. 2, the first-order plots for both trans–cis photoisomerization reactions of BFIAB in HSA– and BSAC–toluene gels upon irradiation with 450 nm-light at initial stage were found to be linear. The Φ_t values in these gels estimated from the slope of the plots were 0.29 ± 0.02 , being almost the same as that in toluene solution within experimental error ($\Phi_t = 0.29$) (23).

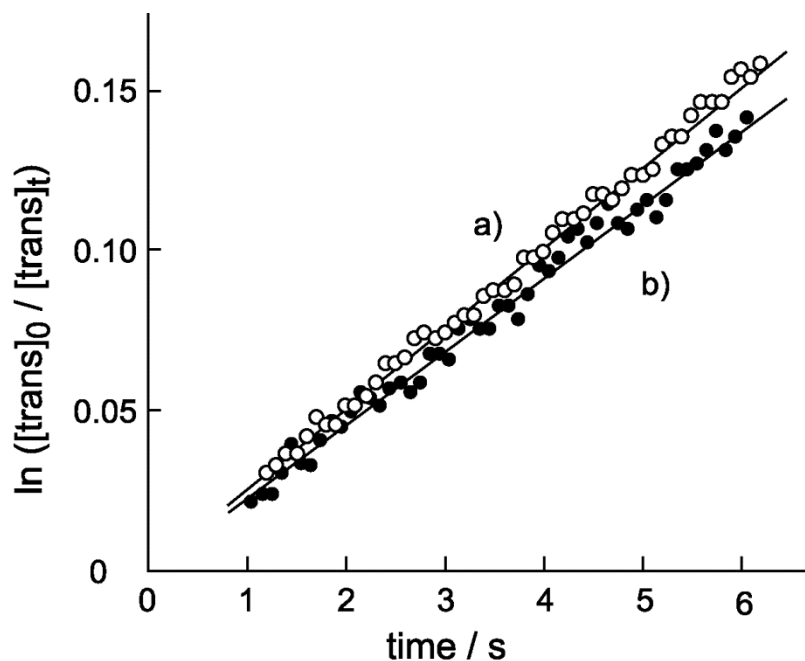


FIGURE 2 First-order plots for trans–cis photoisomerization of BFIAB. a) HSA–toluene gel (HSA: 50 mg mL^{−1}). b) BSAC–toluene gel (BSAC: 5 mg mL^{−1}).

In the present experimental conditions, cis–trans photoisomerization was took place simultaneously with the trans–cis photoisomerization upon irradiation with 450-nm light, and following Eq. (3) can be established when the incident light is intense enough to neglect the contribution of the backward cis–trans thermal isomerization during photoirradiation (23);

$$Y_{\text{pss}} = [1 + (\epsilon_{\text{c}} / \epsilon_{\text{t}}) (\Phi_{\text{c}} / \Phi_{\text{t}})]^{-1} \quad (3)$$

where Φ_{c} is the quantum yield for cis–trans photoisomerization upon irradiation with 450 nm-light. Since the values Y_{pss} and Φ_{t} in the gels were identical to those in toluene solution, the values Φ_{c} in both HSA– and BSAC–toluene gels were also identical to that in toluene solution (0.31). Thus, the three dimensional network constructed by the gelator molecules did not affect the photoisomerization reactions of BFIAB in the solution region of the gels.

Photogenerated cis-isomers of BFIAB exhibits backward thermal cis–trans isomerization reactions. Thus in the next stage, the thermal cis–trans isomerization reactions of BFIAB after the system reached photostationary state were investigated. As shown in Fig. 3, the reactions in the HSA– and BSAC–toluene gels followed the first-order kinetics but the rate constants estimated by the slope of the first-order plot were found to depend upon the kind of gelator; that is, the rate constant in the HSA– toluene gel was larger than that in BSAC–toluene gels.

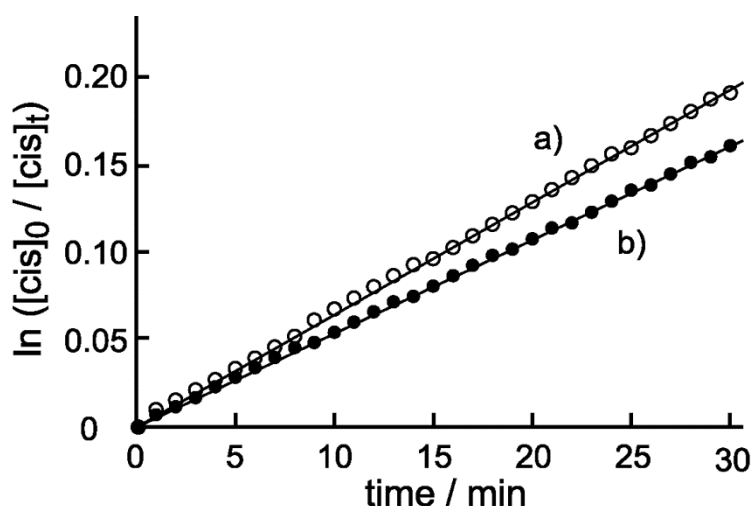


FIGURE 3 First-order plots for backward cis–trans thermal isomerization of BFIAB. a) HSA–toluene gel (HSA: 50 mg mL⁻¹). b) BSAC–toluene gel (BSAC: 5 mg mL⁻¹).

Table 1 summarizes the first-order rate constant (*k*) of thermal cis–trans isomerization reactions of BFIAB together with other parameters for trans–cis and cis–trans photoisomerizations described above.

TABLE 1 Parameters for photochromic reactions of BFIAB.

system	Y_{pss}	$\Phi_{\text{t-c}}$	$\Phi_{\text{c-t}}$	$k / 10^{-3} \text{ min}^{-1}$
HSA—toluene gel ^a	0.74 (0.01)	0.29 (0.02)	0.31	6.2 (0.3)
BSAC—toluene gel ^b	0.74 (0.01)	0.29 (0.02)	0.31	5.4 (0.2)
toluene solution	0.74 (0.01)	0.29 (0.02)	0.31	5.5 (0.2)

Y_{pss} : The fraction of the photogenerated cis-isomer at the photostationary state upon irradiation with 450 nm-light together with the estimated standard deviation in parenthesis. $\Phi_{\text{t-c}}$: Quantum yield for trans–cis photoisomerizations together with the estimated standard deviation in parenthesis. $\Phi_{\text{c-t}}$: Quantum yields for cis–trans photoisomerizations estimated from the values Y_{pss} and $\Phi_{\text{t-c}}$. k : The first-order rate constant of thermal cis–trans isomerization reactions of BFIAB at 30 °C together with the estimated standard deviation in parenthesis.

^aHSA: 50 mg mL⁻¹. ^bBSAC: 5 mg mL⁻¹.

It was found that the rate constant for the HSA—toluene gel was larger than that for toluene solution while that for the BSAC—toluene gel was the same as that for toluene solution. The results suggested that a small fraction of HSA molecules did not embedded in the gel network but existed in the solution region and such molecules in the solution region affected the thermal cis–trans isomerization reactions of BFIAB. It is conceivable that HSA molecule in the solution region functioned as a catalyst for thermal cis–trans isomerization, that is, proton from HSA molecule in solution region was added to the nitrogen atom in cis-BFIAB molecule, which might help the rotation and/or inversion around the N-N bond resulting in acceleration of the thermal cis–trans isomerization reactions of BFIAB. It was found that the rate constant in toluene solution in the presence of 50 mg mL⁻¹ of stearic acid, where the system was not in the gel state but in the clear solution, was $8.1 \times 10^{-4} \text{ min}^{-1}$. The

value of the rate constant was larger than that in toluene solution without stearic acid molecules, suggesting that aliphatic acids function as a catalyst of thermal cis–trans isomerization reactions of BFIAB. With regard to BSAC–toluene gel, it is thought that a small fraction of BSAC molecules also existed in the solution region, however, BSAC did not act as an acid so that the acceleration of the reaction did not observed in the gel.

CONCLUSION

In order to gain information about the environment at solution region within low molecular-mass organogels, photochromic reactions of BFIAB in HSA– and BSAC–toluene gels have been investigated. It was found that BFIAB exhibited photochromism in these gels as well as in solution and trans–cis and cis–trans photoisomerization reactions were quite similar to those in toluene solution, suggesting that the network constructed by the gelator molecules did not affect the photoisomerization reactions. With regard to thermal cis–trans isomerization, the reaction was found to be accelerated in HSA–toluene gel system, suggesting that a small fraction of gelator molecules did not embedded in the gel network but existed in the solution region within the gels. The present study showed that the environment at the solution region within the gels was essentially the same as that in the usual solution for photochromic reactions of BFIAB although a small fraction of gelator molecules were existed in the solution region. Thus the present study may promise that the low molecular-mass organogels including functional molecules in the solution region provide apparent solid materials with excellent functionality comparable to that in solution, whereas embedding the functional materials in the bulk solids such as polymers often causes the decline in function. It is however expected that features of bimolecular reactions, molecular diffusion, polarized light induced anisotropy, etc. in these gels are different from those observed in solution due to slow dynamics in the gels. Further investigation to elucidate

such properties related to slow dynamics in low molecular-mass organogels are in progress.

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