Photochromic Behavior in the Molecular Glass of 4,4',4''-Tris(3-methylphenyphenylamino)triphenylamine

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For the purpose of gaining information on the microstructure of molecular glasses, photochromic behavior of 4-dimethylaminoazobenzene (DAAB) in the molecular glass of 4,4',4"-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA) was studied in comparison with that in a polystyrene matrix and in a benzene solution. The results strongly suggest that the local free volume in the molecular glass of *m*-MTDATA is smaller than that in the polystyrene glass.

Low molecular-weight organic glasses, *i.e.*, molecular glasses, are of interest as a novel class of organic materials.[1-8] They have found a successful application as materials for use in organic electroluminescent devices.[6-8] In addition, molecular glasses are expected to function as a novel type of host matrices for embedding a variety of functional materials. It is of importance to clarify the properties of molecular glasses as host matrices and to understand how the microstructure of molecular glasses is different from that of polymer glasses. Photochromic reactions in host matrices are expected to serve as a probe for gaining information on the microstructure of the host matrix in the light of previous studies dealing with photochromic reactions in polymer glasses, which have been discussed in terms of molecular motions associated with glass transition and free volume of host polymer matrices.[9-17]

In the present study, we have investigated photochromic behavior of 4-dimethylaminoazobenzene (DAAB) in the molecular glass of 4,4',4"-tris(3-methylphenylphenylamino)-triphenylamine (*m*-MTDATA)[1] as a host matrix in comparison with that in a polystyrene matrix and in a benzene solution in order to gain information on the microstructure of molecular glasses as well as to elucidate the properties of molecular glasses as novel host matrices for photochromic reactions.

Films with molar ratios of *m*-MTDATA : DAAB = 3:1 and 100:1 (which are abbreviated hereafter as 3:1- and 100:1-*m*-MTDATA films, respectively) were prepared on a transparent glass substrate by a spin-coating method using a benzene solution of *m*-MTDATA and *trans*-DAAB. Both films were found to be amorphous, as confirmed by X-ray diffraction and polarizing microscopy (Tg = 60 and 71 °C for 3:1- and 100:1-*m*-MTDATA films, respectively). A film of polystyrene (n=1600-1800, Wako Pure Chem. Ind., Ltd.) containing the same DAAB concentration as that in the 100:1-*m*-MTDATA film (0.28 wt%) was also prepared by a spin-coating method (Tg = 95 °C for the polystyrene film containing DAAB).

Reversible *trans-cis* photoisomerization of DAAB took place in the *m*-MTDATA glass. Upon irradiation with 400 nm-light from a 500 W Xenon lamp (UXL-500D, USHIO) through an interference filter (IF-S 400, Vacuum Optics Co.), the absorbance around 410 nm decreased due to the photoisomerization of *trans*-DAAB to the *cis*-form for both 3:1- and 100:1-*m*-MTDATA films (Figure 1). When irradiation was stopped after the reaction system had reached a photostationary state, the absorption spectrum of the film gradually recovered to the original one due to the backward thermal *cis-trans* isomerization of DAAB. The *cis*-fraction of DAAB at the photostationary state at 30 °C was estimated to be *ca.* 0.54 and 0.26 for the 3:1- and 100:1-*m*-MTDATA films, respectively, based on the absorbance of the films at 405 nm and the molar extinction coefficients of *trans*-DAAB,[18] *cis*-DAAB,[18] and *m*-MTDATA ($\varepsilon_{trans\text{-DAAB}} = 2.8 \times 10^4$, $\varepsilon_{cis\text{-DAAB}} = 2.0 \times 10^3$, $\varepsilon_{m\text{-MTDATA}} = 6.2 \times 10^2$). The values of the *cis*-fraction of DAAB at the photostationary state in the *m*-MTDATA glass were smaller than those (*ca.* 0.85) for the benzene solution and the polystyrene film. That is, a large number of *trans*-DAAB molecules remain unchanged probably because local free volume around the remaining *trans*-DAAB molecules is not large enough to allow the isomerization from the *trans*-DAAB to the *cis*-form in the *m*-MTDATA glass matrix.

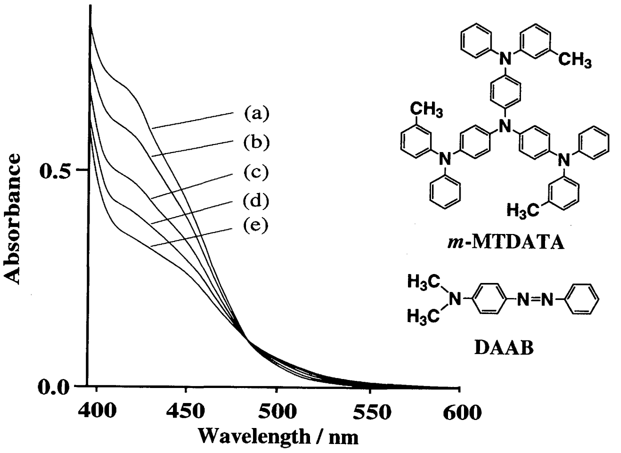

Figure 1. Electronic absorption spectra of 3:1-*m*-MTDATA film. (a) before irradiation, irradiated with 400 nm-light for (b) 2 min., (c) 5 min., and (d) 10 min., and (e) photostationary state.

The apparent rate constant at the initial stage of the backward thermal *cis-trans* isomerization of DAAB in the *m*-MTDATA glass was found to be considerably larger than those in the polystyrene matrix and in the benzene solution. Figure 2 shows the first-order plots for the thermal *cis-trans* isomerization of the 3:1- and 100:1-*m*-MTDATA films at 30 °C after the reaction system has reached the photostationary state upon irradiation with 400 nm-light. The results of the benzene solution (3.3 x 10^{-4} mol dm^{-3}) and the polystyrene glass matrix are also shown in Figure 2. It was found that the backward thermal *cis-trans* isomerization of DAAB in the *m*-MTDATA glass does not follow the first-order kinetics in contrast to the reaction in the benzene solution which follows the first-order kinetics. The slopes of the first-order plots, *i.e.*, the apparent rate constants, for the backward thermal *cis-trans* isomerization of the 3:1- and 100:1-*m*-MTDATA films are initially much larger than those in the benzene solution and the polystyrene film, gradually approaching

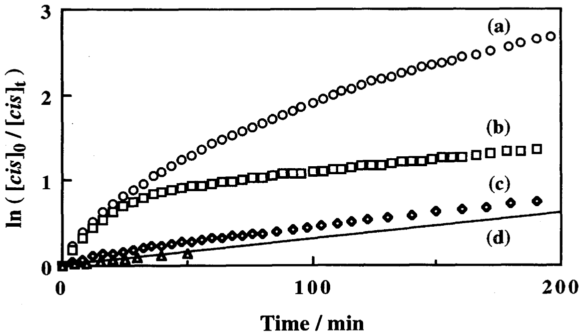

Figure 2. First-order plots for the thermal *cis-trans* isomerization of DAAB in (a) 3:1-*m*-MTDATA film, (b) 100:1-*m*-MTDATA film, (c) polystyrene film, and (d) benzene solution.

the same value as that in the solution.

It has been reported that the thermal *cis-trans* isomerizations of azobenzene derivatives embedded in polymer matrices and azobenzene moieties attached to polymers do not follow simple first-order kinetics, involving a faster component relative to the reaction in solution[9-12,14,17] and that these phenomena are due to the existence of the *cis*-isomer trapped in a strained conformation in the host polymer matrix, which goes back faster into the *trans*-isomer than the structurally relaxed *cis*-isomer, which is isomerized at the same rate as that in solution.[9,14]

The backward thermal *cis-trans* isomerization of DAAB in the *m*-MTDATA glass did not follow the Kohlrausch-Williams-Watts function ($[cis]_t / [cis]_0 = \exp[-(t/\tau)^\beta]$)[19] either; however, the reaction of the 100:1-*m*-MTDATA film was successfully analyzed in terms of the first-order kinetics consisting of two components, according to eq. 1;

$$[cis]_t / [cis]_0 = f_1 \exp(-k_1 t) + f_2 \exp(-k_2 t) \qquad (1)$$

where $[cis]_0$ and $[cis]_t$ are the concentrations of *cis*-DAAB at the initial stage and at time t, respectively, f_1 and f_2, and k_1 and k_2 represent the fractions and the rate constants for the faster and slower components, respectively. Table 1 lists the kinetic parameters for the reactions in the *m*-MTDATA glass, the polystyrene matrix, and the benzene solution. The faster and slower components are thought to be attributed to the reactions of the strained *cis*-isomer and structurally relaxed one, respectively. It is notable that the fraction of the faster component in the 100:1-*m*-MTDATA film (f_1=0.54) was considerably larger than that in the polystyrene matrix film (f_1=0.12); this leads to the considerably faster apparent rate constant at the initial stage for the 100:1-*m*-MTDATA film than for the polystyrene matrix film. These results indicate that the ratio of the strained *cis*-isomer to the relaxed one formed in the 100:1-*m*-MTDATA film at the photostationary state is much larger than that in the polystyrene film. Regarding the 3:1-*m*-MTDATA film, the reaction could not be analyzed by eq. 1 probably due to the involvement of more than two components with different rate constants or due to the gradual change of the microenvironment around the remaining *cis*-isomer along with the progress of the reaction; however, the apparent rate constant even at the time when more than 90% of the reaction has proceeded is still larger than those in the polystyrene matrix and in the benzene solution. It is suggested that most *cis*-isomers photochemically generated in the 3:1-*m*-MTDATA film take strained conformations. It has been reported that the molar extinction coefficients of the n-π^* bands for *trans*-azobenzenes with bent conformations, *e.g.*, [2.2](4,4')-azobenzenophane,[20] and for azobenzene derivatives entrapped in silica-gel glasses[21] are larger than those for *trans*-azobenzenes with planar structures due to the increase in the degree of mixing of the n-orbital with the π-orbital in a bent conformation. However, no such change was observed with regard to *cis*-DAAB in the *m*-MTDATA films and the polystyrene film.

Table 1. Kinetic parameters in eq. 1 for the thermal *cis-trans* isomerization of DAAB at 30 °C

	k_1 / min^{-1}	f_1	k_2 / min^{-1}	f_2
100:1-*m*-MTDATA film	0.083	0.54	0.003	0.46
polystyrene matrix	0.062	0.12	0.003	0.88
benzene solution[a]	–	–	0.003	1.00

[a] single component

The present study presents the important results regarding the properties and the microstructure of the molecular glass as a novel host matrix. It is shown that the fraction of the photoisomerized *cis*-isomer at the photostationary state in the *m*-MTDATA matrix is smaller than that in the polystyrene matrix and that the apparent rate constant at the initial stage for the backward thermal *cis-trans* isomerization of DAAB in the *m*-MTDATA glass is considerably larger than those in the polystyrene matrix and in the benzene solution. These results indicate that there is a great difference in the size and distribution of local free volume between the molecular glass of *m*-MTDATA and the polystyrene matrix; the local free volume in the molecular glass of *m*-MTDATA is suggested to be smaller than that in the polystyrene glass. Further studies extending to other photochromic compounds and molecular glasses are underway.

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