Photochromism of Dimethylaminoazobenzene in a Molecular Glass of 4,4',4''-Tri(*N*-carbazolyl)triphenylamine

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Amorphous organic polymers have been widely used as host matrices for embedding a variety of functional molecules, due to their film-forming capability, transparency, and isotropic and homogeneous properties. Low molecular-weight organic compounds that readily form amorphous glasses above room temperature, which we refer to as "molecular glasses" or "amorphous molecular materials", are also expected to function as host matrices. However, no such study has been made because low molecular-weight organic compounds generally tend to crystallize readily. We have created several novel families of amorphous molecular materials,[1-21] and investigated the photochromic reaction of 4-dimethylaminoazobenzene (DAAB) in the molecular glass of 4,4',4''-tris(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA).[13] Studies of photochromic reactions in the host matrix are also of interest in that they serve as a probe for gaining information on the microstructure of the host matrix.

In the present study, we have investigated photochromic behavior of DAAB in the molecular glass of 4,4',4''-tri(*N*-carbazolyl)triphenylamine (TCTA) as a novel host matrix in order to gain information on the microstructure of the molecular glass as well as to elucidate the properties of the molecular glass as novel host matrix for photochromic reactions.

TCTA was synthesized as described in our previous paper.[10] DAAB was obtained commercially (Tokyo Chemical Industry, Co., Ltd.) and purified by sublimation (*ca.* 80 °C, 0.15

mmHg). TCTA films containing DAAB in the molar ratios of 3:1 and 100:1 (TCTA:DAAB), which are abbreviated hereafter as 3:1- and 100:1-TCTA films, respectively, were prepared on a transparent glass substrate by the spin-coating method using a benzene solution of TCTA and *trans*-DAAB. Both films were found to be amorphous, as confirmed by differential scanning calorimetry, X-ray diffraction, and polarizing microscopy (T_g : 114 and 147 °C for 3:1- and 100:1-TCTA films, respectively).

Reversible photoisomerization of DAAB took place in the TCTA glass. Upon irradiation of both the 3:1- and 100:1-TCTA films 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 of the electronic absorption band with λ_{max} at 410 nm decreased

due to the photoisomerization of *trans*-DAAB to the *cis*-form (Fig. 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.

Fig. 1. Electronic absorption spectra of 3:1-TCTA film. (a) before irradiation; (b)-(e) irradiated with 400 nm-light for (b) 2 min., (c) 5 min., and (d) 10 min., and (e) longer than 20 min. (photostationary state).

The *cis*-fraction of DAAB at the photostationary state at 30 °C was estimated to be *ca.* 0.51 and 0.27 for the 3:1- and 100:1-TCTA films, respectively, based on the absorbance of the films at 405 nm and the molar extinction coefficients of *trans*- and *cis*-DAAB ($\epsilon_{trans\text{-DAAB}} = 2.8 \times 10^4$, $\epsilon_{cis\text{-DAAB}} = 2.0 \times 10^3$).^[22] These values, which are similar to those of the *m*-MTDATA glass (0.54 and 0.26 for 3:1- and 100:1-*m*-MTDATA films, respectively^[13]), were smaller than those (*ca.* 0.85) for the benzene solution and the polystyrene film. These results indicate that a large number of *trans*-DAAB molecules remain unchanged in these molecular glass matrices probably because the 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. The size of local free volume in the *m*-MTDATA and TCTA host matrices is suggested to be smaller than that in the polystyrene glass.

As observed for the *m*-MTDATA glass, the

apparent rate constant at the initial stage of the backward thermal *cis*→*trans* isomerization of DAAB in the TCTA glass was found to be larger than those in the polystyrene matrix and in the benzene solution. Fig. 2 shows the first-order plots for the thermal *cis*→*trans* isomerization of the 100:1-TCTA film at 30 °C after the reaction system has reached the photostationary state upon irradiation with 400 nm-light, together with those for the benzene solution (3.3×10^{-4} mol dm⁻³) and the polystyrene glass matrix. The results show that in contrast to the reaction in the benzene solution which follows the first-order kinetics, the backward thermal *cis*→*trans* isomerization of DAAB in the TCTA glass does not follow the first-order kinetics. The slope of the first-order plots, *i.e.*, the apparent rate constant, for the backward thermal *cis*→*trans* isomerization of the 100:1-TCTA film is initially much larger than those for the benzene solution and the polystyrene film, gradually approaching the same value as that in the solution.

Fig. 2. First-order plots for the thermal *cis*→*trans* isomerization of DAAB. (a) 100:1-TCTA film (b) polystyrene film. (c) benzene solution.

Like the case of the 100:1-*m*-MTDATA film, the reaction of the 100:1-TCTA film could be analyzed in terms of eq. 1, the first-order kinetics consisting of two components;

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

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 TCTA glass, the *m*-MTDATA glass, the polystyrene matrix, and the benzene solution. The rate constant of the slower component for the TCTA,

m-MTDATA, and polystyrene films was equal to the rate constant for the benzene solution; this indicates that the slower component is attributed to the reaction of the structurally relaxed *cis*-isomer. On the other hand, the faster component is thought to be attributed to the reaction of the photogenerated *cis*-isomer with a strained conformation due to the presence of the surrounding matrix which restricts the molecular motion of DAAB. Similar phenomena have also been reported for a few polymer systems.[23,24] It was found that the fractions of the faster component for the *m*-MTDATA and TCTA films were considerably larger than that for the polystyrene matrix film; this leads to the faster apparent rate constant at the initial stage for the *m*-MTDATA and TCTA films than for the polystyrene matrix film. These results indicate that the ratio of the strained *cis*-isomer to the relaxed one formed in the molecular glasses at the photostationary state is much larger than that in the polystyrene film. It is suggested that the local free volume in the molecular glasses is smaller than that in the polystyrene glass.

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
TCTA film	0.032	0.35	0.003	0.65
<i>m</i> -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

^asingle component

In summary, photochromism of DAAB in the molecular glass of TCTA was investigated in order to gain information on the microstructure of the molecular glass as well as to elucidate the properties of the molecular glass as a novel host matrix. It was shown that the fraction of the photoisomerized *cis*-isomer at the photostationary state is smaller in the TCTA matrix than 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 TCTA glass is larger than those in the polystyrene matrix and in the benzene solution. These results suggest that the local free volume in the molecular glass is smaller than that in the polystyrene glass.

References

1. Y. Shirota, T. Kobata, and N. Noma, *Chem. Lett.*, (1989) 1145.
2. W. Ishikawa, H. Inada, H. Nakano, and Y. Shirota, *Chem. Lett.*, (1991) 1731.
3. K. Nishimura, T. Kobata, H. Inada, and Y. Shirota, *J. Mater. Chem.*, **1** (1991) 897.
4. A. Higuchi, H. Inada, T. Kobata, and Y. Shirota, *Adv. Mater.*, **3** (1991) 549.
5. W. Ishikawa, H. Inada, H. Nakano, and Y. Shirota, *Mol. Cryst. Liq. Cryst.*, **211** (1992) 431.
6. H. Inada and Y. Shirota, *J. Mater. Chem.*, **3** (1993) 319.
7. W. Ishikawa, K. Noguchi, Y. Kuwabara, and Y. Shirota, *Adv. Mater.*, **5** (1993) 559.
8. H. Inada, K. Ohnishi, S. Nomura, A. Higuchi, H. Nakano, and Y. Shirota, *J. Mater. Chem.*, **4** (1994) 171.
9. Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, and K. Imai, *Appl. Phys. Lett.*, **65** (1994) 807.
10. Y. Kuwabara, H. Ogawa, H. Inada, N. Noma, and Y. Shirota, *Adv. Mater.*, **6** (1994) 677.
11. E. Ueta, H. Nakano, and Y. Shirota, *Chem. Lett.*, (1994) 2397.
12. H. Kageyama, K. Itano, W. Ishikawa, and Y. Shirota, *J. Mater. Chem.*, **6** (1996) 675.
13. H. Nakano, K. Akamatsu, K. Moriwaki, and Y. Shirota, *Chem. Lett.*, (1996) 701.
14. M. Yoshiiwa, H. Kageyama, F. Wakasa, M. Takai, K. Gamo, and Y. Shirota, *Appl. Phys. Lett.*, **69** (1996) 2605.
15. S. Nomura and Y. Shirota, *Chem. Phys. Lett.*, **268** (1997) 461.
16. T. Noda, H. Ogawa, N. Noma, and Y. Shirota, *Adv. Mater.*, **9** (1997) 720.
17. K. Itano, T. Tsuzuki, H. Ogawa, S. Appleyard, M. R. Willis, and Y. Shirota, *IEEE Transactions on Electron Devices*, **44** (1997) 1218.
18. H. Kageyama, K. Ohnishi, S. Nomura, and Y. Shirota, *Chem. Phys. Lett.*, **277** (1997) 137.
19. J. Sakai, H. Kageyama, S. Nomura, H. Nakano, and Y. Shirota, *Mol. Cryst. Liq. Cryst.*, **296** (1997) 445.
20. K. Itano, H. Ogawa, and Y. Shirota, *Appl. Phys. Lett.*, **72** (1998) 636.
21. K. Katsuma and Y. Shirota, *Adv. Mater.*, **10** (1998) 223.
22. E. Fischer and Y. Frei, *J. Chem. Phys.*, **27** (1957) 328.
23. C. S. Paik and H. Morawetz, *Macromolecules*, **5** (1972) 171.
24. I. Mita, K. Horie, and K. Hirao, *Macromolecules*, **22** (1989) 558.