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Photochromic reaction in a molecular glass as a novel host matrix: the 4-dimethylaminoazobenzene–4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine system

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For the purposes of clarifying the properties of a molecular glass as a novel host matrix and gaining information on the microstructure of the molecular glass, the photochromic behavior of 4-dimethylaminoazobenzene (DAAB) in a novel molecular glass of 4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (*m*-MTDATA) was investigated, and compared with its behavior in a polystyrene glass matrix and a benzene solution. It was found that the fraction of the photoisomerized *cis*-isomer of DAAB at the photostationary state is smaller in the *m*-MTDATA glass matrix than in the polystyrene matrix and the benzene solution, and that the apparent initial rate constant for the backward *cis*→*trans* thermal isomerization of DAAB is much larger in the *m*-MTDATA glass than in the polystyrene matrix and the benzene solution. These results suggest that the average size of local free volume in the molecular glass of *m*-MTDATA is smaller than that in the polystyrene glass.

Amorphous glasses serve as excellent host matrices because of their excellent film formation, transparency, isotropic properties, and homogeneous properties owing to the absence of grain boundaries. Inorganic sol-gel glasses have been widely used as host matrices, embedding a variety of functional materials. Organic polymers have also been widely used as matrices for embedding functional materials. For example, molecularly-doped polymer systems where photoconducting materials are dispersed in an amorphous polymer such as polycarbonate have been put to practical use as photoreceptors in electrophotography. Photochromic reactions of low molecular-weight organic compounds dispersed in a polymer matrix have also been studied extensively, and microenvironmental effects on photochromic reactions have been discussed in terms of their molecular motions associated with glass transition and the free volume of host polymer matrices.[1–11]

In contrast to polymers, low molecular-weight organic compounds tend to crystallize readily. We have been making studies of the creation of low molecular-weight organic compounds that readily form stable amorphous glasses above room temperature, which we refer to as ‘amorphous molecular materials’ or ‘molecular glasses’, considering the following aspects. Amorphous molecular materials are expected to constitute a novel family of organic functional materials that exhibit glass-transition phenomena usually associated with polymers. Creating such amorphous molecular materials is of interest and significance not only for technological applications but also from a scientific viewpoint, opening up a new field of organic materials science that deals with ‘molecular glasses’. We have created several novel families of molecular glasses with relatively high glass-transition temperatures (T_gs), which include 4,4′,4″-tris(diphenylamino)triphenylamine (TDATA) and its derivatives,[12–16] substituted 1,3,5-tris(diphenylamino)benzenes (TDABs),[17–24] 4,4′,4″-tris(diphenylamino)triphenylbenzene (TDAPB) and its derivatives,[25] and others.[26–31] They readily form uniform amorphous films by vacuum deposition, spin coating or solvent casting and have found successful application as materials for organic electroluminescent devices.[14–16,32–36] Like polymers, molecular glasses are also expected to function as novel host matrices for embedding functional materials such as photochromic materials. It is of interest to elucidate the properties of molecular glasses as host matrices in comparison with those of amorphous polymers. In addition, studies of photochromic reactions in the molecular glass are expected to provide information on the microstructure of the molecular glass as the host matrix.

In the present study, we have investigated photochromic reactions in a molecular glass of 4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (*m*-MTDATA) in order to elucidate the properties of the molecular glass as a novel host matrix and to gain information on the microstructure of the molecular glass. An azobenzene derivative was chosen as a photochromic compound because azobenzenes have been most extensively studied. Since the *m*-MTDATA film shows an electronic absorption band in the near UV region, we selected 4-dimethylaminoazobenzene (DAAB) as a photochromic probe compound, which shows an absorption spectral change due to *trans*↔*cis* isomerization in the visible region. The photoisomerization behavior and the kinetics for the backward *cis*→*trans* thermal isomerization of DAAB in the molecular glass of *m*-MTDATA are investigated in the temperature region below and above the T_g. The results are discussed in comparison with those in a polystyrene matrix and a benzene solution. Preliminary results have been reported as a communication.[37]

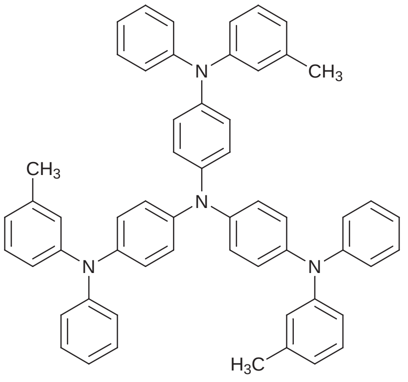
Experimental

Materials

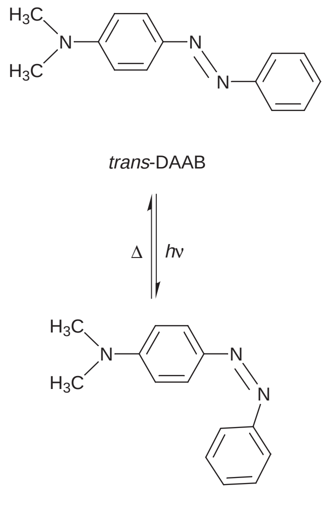
m-MTDATA was prepared according to the method described in our previous paper.[12] *trans*-DAAB was obtained commercially (Tokyo Chemical Industry, Co., Ltd.) and purified by sublimation (at *ca.* 80 °C and at 0.15 mmHg). Polystyrene was commercially available (Wako Pure Chem. Ind., Ltd.) and purified by repeated reprecipitation from benzene into methanol ($M_w = 1.9 \times 10^5$, $M_w/M_n = 1.7$).

Preparation of glass samples for DSC measurement

Glass samples for the determination of T_g by differential scanning calorimetry (DSC) were prepared as follows. Appropriate amounts of *m*-MTDATA and *trans*-DAAB with molar ratios of *m*-MTDATA : DAAB = 3 : 1, 5 : 1, 10 : 1 and



m-MTDATA



trans-DAAB

cis-DAAB

100 : 1, were placed in a glass sample tube, and then the tube was sealed off. After the sample melted on heating in the sample tube, it was allowed to cool to room temperature to give a homogeneous glass of *m*-MTDATA containing DAAB.

Photochromic reaction in amorphous films

Amorphous films of *m*-MTDATA containing *trans*-DAAB were prepared on a transparent glass substrate by spin coating from a benzene solution containing appropriate amounts of *m*-MTDATA and DAAB. The film was dried overnight under reduced pressure before use. The resulting film was confirmed to be amorphous by X-ray diffraction and polarizing microscopy. Polystyrene films containing DAAB were also prepared by spin coating from a benzene solution.

Photoisomerization of DAAB in the amorphous films of *m*-MTDATA and polystyrene was carried out by irradiation with 400 nm light with a bandwidth of 10 nm from a 500 W Xenon lamp (UXL-500D, USHIO) through an interference filter (IF-S 400, Vacuum Optics Co.) and an optical fiber. Photochromic reactions were analyzed from the change in the electronic absorption spectra.

Apparatus

T_g values were determined by DSC with a Seiko DSC220C. Electronic absorption spectral change were measured with a Hitachi U-3200 spectrophotometer. The sample was kept at a constant temperature by using a temperature controller (TM-105, Toho Electronics Inc.) with a tungsten heater.

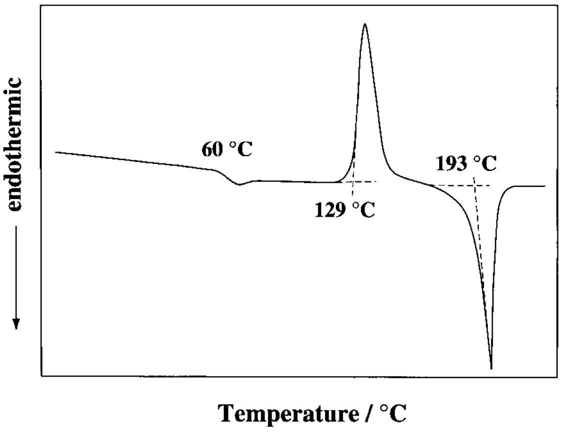


Fig. 1 DSC curve of a glass obtained by cooling the melt of a mixture of *m*-MTDATA and DAAB with a molar ratio of *m*-MTDATA : DAAB = 3 : 1.

Results and discussion

Glass formation of DAAB—*m*-MTDATA mixtures

It was found that the mixtures of varying amounts of *m*-MTDATA and DAAB form homogeneous, amorphous glasses, as confirmed by DSC, X-ray diffraction, and polarizing microscopy. Fig. 1 shows a DSC curve of a glass obtained by cooling the melt of the mixture of a molar ratio of *m*-MTDATA : *trans*-DAAB = 3 : 1. When the sample was heated, a glass-transition phenomenon was observed at 60 °C, which was 15 °C lower than the T_g of *m*-MTDATA itself. The result that only one glass-transition phenomenon was observed suggests that the DAAB molecules are homogeneously dispersed in the *m*-MTDATA glass matrix. On further heating, an exothermic peak due to crystallization of both *m*-MTDATA and DAAB was observed at *ca.* 129 °C, followed by a broad endothermic peak due to melting at around 193 °C. The X-ray diffraction (XRD) pattern of a glass with a molar ratio of *m*-MTDATA : *trans*-DAAB = 3 : 1 is shown in Fig. 2. No appreciable difference in the XRD pattern was observed among the glasses with varying molar ratios of *m*-MTDATA and DAAB. Table 1 lists the T_gs of the glasses of the mixtures of

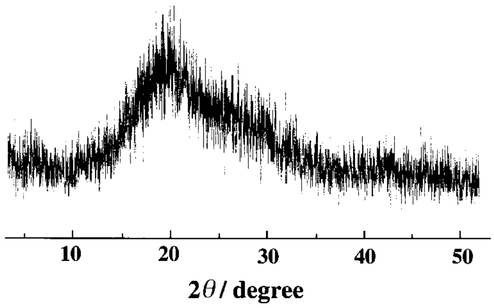


Fig. 2 X-Ray diffraction pattern of a glass obtained by cooling the melt of a mixture of *m*-MTDATA and DAAB with a molar ratio of *m*-MTDATA : DAAB = 3 : 1.

Table 1 Glass-transition temperatures (T_gs) of the glasses of mixtures of *m*-MTDATA and DAAB

Sample	T_g/°C
m-MTDATA	75
m-MTDATA : DAAB = 100 : 1[a]	71
m-MTDATA : DAAB = 10 : 1[a]	63
m-MTDATA : DAAB = 5 : 1[a]	60
m-MTDATA : DAAB = 3 : 1[a]	60

[a] Molar ratio.

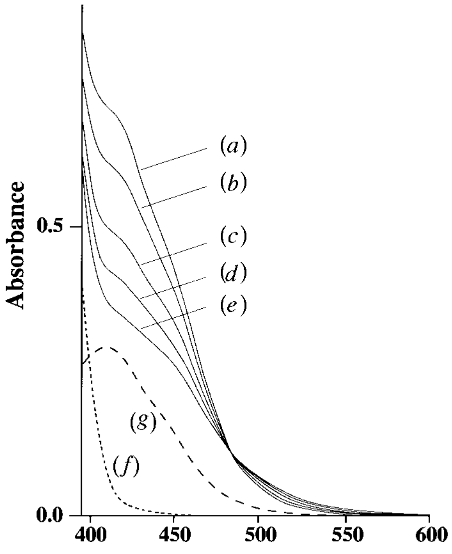


Fig. 3 Electronic absorption spectral change of 3 : 1-*m*-MTDATA film: (*a*) before irradiation; (*b*)–(*e*) irradiated with 400 nm light for (*b*) 2, (*c*) 5, (*d*) 10 and (*e*) longer than 30 min (photostationary state). Electronic absorption spectra of (*f*) an amorphous film of *m*-MTDATA alone and (*g*) DAAB in a benzene solution (1.0×10^{-5} mol dm^{-3}).

m-MTDATA and DAAB. It was found that the T_g decreases as the concentration of DAAB increases.

Photochromism of DAAB in the *m*-MTDATA glass matrix

The amorphous film with a molar ratio of *m*-MTDATA : DAAB = *n* : 1 prepared on a transparent glass substrate by spin coating from a benzene solution is hereafter referred to as the *n* : 1-*m*-MTDATA film (*n* = 3, 5, 10, 100). The reversible *trans*→*cis* and *cis*→*trans* photoisomerizations and thermal isomerizations of DAAB took place in the *n* : 1-*m*-MTDATA amorphous film. Fig. 3 shows the electronic absorption spectral change for the 3 : 1-*m*-MTDATA film together with the electronic absorption spectra of an amorphous film of *m*-MTDATA alone, prepared on a glass substrate by spin coating from a benzene solution, and *trans*-DAAB in a benzene solution. Upon irradiation with 400 nm light, the absorbance of the film at around 410 nm decreased due to the photoisomerization of *trans*-DAAB to the *cis*-form. When irradiation was stopped after the reaction system had reached a photostationary state, the absorption spectrum of the film gradually began to recover to give the original one due to the backward thermal isomerization of *cis*-DAAB to the *trans*-form. The *m*-MTDATA film was stable to 400 nm light irradiation under the same conditions.

The *cis*-fraction (*Y*) of DAAB in the *n* : 1-*m*-MTDATA film at the photostationary state can be determined from eqn. (1),

$$Y = \left(\frac{\varepsilon_t + n\varepsilon_h}{\varepsilon_t - \varepsilon_c}\right)\left(\frac{A_{int} - A_{pss}}{A_{int}}\right) \qquad (1)$$

where ε_t, ε_c and ε_h are the molar extinction coefficients of *trans*-DAAB ($\varepsilon_t = 2.9 \times 10^4$ M^{-1} cm^{-1} at 405 nm),[38] *cis*-DAAB ($\varepsilon_c = 2.0 \times 10^3$ M^{-1} cm^{-1} at 405 nm),[38] and the *m*-MTDATA host matrix ($\varepsilon_h = 6.2 \times 10^2$ M^{-1} cm^{-1} at 405 nm), and A_{int} and A_{pss} are the absorbances of the film at the initial and photostationary states, respectively. Table 2 shows the *Y* values for the *n* : 1-*m*-MTDATA films at 30 °C. It was found that the *cis*-fraction *Y* of DAAB in the *m*-MTDATA glass is smaller than those (*ca.* 0.85) for a polystyrene glass and a benzene solution and that the *Y* value increases when the concentration of DAAB increases in the DAAB—*m*-MTDATA system. The result that the *Y* value for the *m*-MTDATA glass is smaller than those for the polystyrene film and the benzene solution indicates that a number of *trans*-DAAB molecules remain unchanged in the *m*-MTDATA amorphous film, probably because the local free volume around the remaining *trans*-DAAB molecules is not large enough to allow the isomerization of DAAB from its *trans*-form to the *cis*-form in the *m*-MTDATA glass matrix. It is suggested that the average size of local free volume in the *m*-MTDATA glass is smaller than that in the polystyrene glass. The increase in the *Y* value with increasing concentration of DAAB in the *m*-MTDATA glass matrix indicates that the addition of DAAB into the *m*-MTDATA glass causes a change in the microstructure of the glass, *e.g.* the size and distribution of the local free volume. It is suggested that the fraction of the local free volume that allows the photoisomerization of DAAB increases with increasing concentration of DAAB.

Table 2 The *cis*-fraction (*Y*) of DAAB at the photostationary state upon irradiation with 400 nm light at 30 °C in *m*-MTDATA films

Reaction system	*Y*
100 : 1-*m*-MTDATA film	0.26
10 : 1-*m*-MTDATA film	0.48
5 : 1-*m*-MTDATA film	0.54
3 : 1-*m*-MTDATA film	0.54

Next, the backward *cis*→*trans* thermal isomerization of DAAB in the *m*-MTDATA glass was examined. The ratio of the concentration of *cis*-DAAB at the initial state and at time *t* was determined from the absorbance at 410 nm according to eqn. (2),

$$\frac{[cis]_0}{[cis]_t} = \frac{A_0 - A_\infty}{A_t - A_\infty} \qquad (2)$$

where $[cis]_0$ and $[cis]_t$ represent the concentration of *cis*-DAAB at the initial state and at time *t*, respectively, and A_0, A_∞, and A_t are the absorbances of the film at 410 nm at the initial and infinite time, and at a time *t*, respectively. If the reaction follows first-order kinetics, the plots of $\ln([cis]_0/[cis]_t)$ *vs.* time will be linear and the slope of the straight line represents the rate constant for the reaction. Fig. 4 shows the first-order plots for the *cis*→*trans* thermal isomerization of the 3 : 1- and 100 : 1-*m*-MTDATA films at 30 °C after the reaction system has reached the photostationary state by irradiation with 400 nm light. The results for a benzene solution

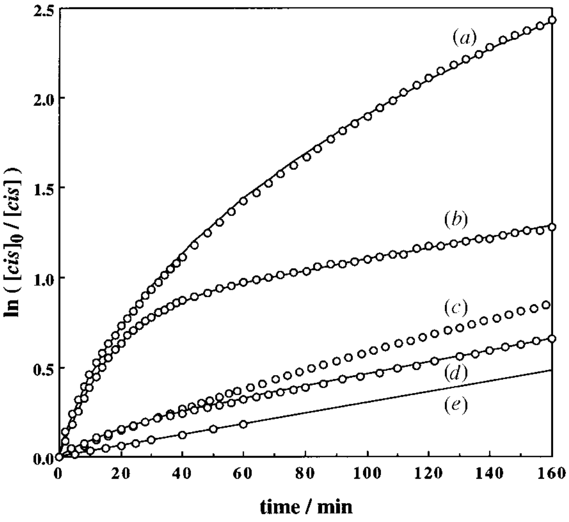


Fig. 4 First-order plots for the *cis*→*trans* thermal isomerization of DAAB in (*a*) 3 : 1-*m*-MTDATA film, (*b*) 100 : 1-*m*-MTDATA film and (*c*) 3 : 1-*m*-MTDATA film prepared under irradiation of 400 nm light, (*d*) polystyrene film and (*e*) benzene solution. Solid lines are fitting curves based on eqn. (3) for (*a*) and eqn. (4) for (*b*), (*d*) and (*e*).

(3.3×10^{-4} mol dm^{-3}) and a polystyrene glass matrix containing the same DAAB concentration as that in the 100 : 1-*m*-MTDATA film (0.28 wt%) are also shown in Fig. 4. It was found that the *cis*→*trans* thermal isomerization of DAAB in the *m*-MTDATA and polystyrene films did not follow first-order kinetics and that the apparent rate constant for the *cis*→*trans* thermal isomerization in the *m*-MTDATA glass is initially much larger than those in the polystyrene matrix and the benzene solution, gradually approaching the same value as that in the solution. This result suggests that there exist *cis*-isomers trapped in strained conformations in the host matrix, which go back faster to the *trans*-isomers than the structurally relaxed *cis*-isomers. In order to verify this idea, the 3 : 1-*m*-MTDATA film was prepared by spin coating under 400 nm light irradiation and the backward *cis*→*trans* thermal isomerization was examined. As a result, the first-order plot for the 3 : 1-*m*-MTDATA film prepared under irradiation showed less deviation from the linear plot [Fig. 4(*c*)] than the film prepared in the dark [Fig. 4(*a*)]. This result indicates that the amount of the strained *cis*-DAAB in the film prepared under irradiation is smaller than that prepared in the dark. Similar phenomena have also been reported for polymer film systems.[3,8]

Kinetic analysis of the *cis*→*trans* thermal isomerization of DAAB in *m*-MTDATA films

Since the *cis*→*trans* thermal isomerization did not follow simple first-order kinetics, the Kohlrausch–Williams–Watts (KWW) function ($[cis]_t/[cis]_0=\exp[-(t/\tau)^\beta]$),[39] the Gaussian Model,[40] and first-order kinetics for a two component system were applied. As a result, the *cis*→*trans* thermal isomerization of DAAB in the 3 : 1-*m*-MTDATA film was successfully analyzed by the Gaussian Model, which assumes a Gaussian distribution of the free energy of activation. In terms of this model, the ratio of the concentration of the *cis*-isomer at a time t to that at the initial time, $[cis]_t/[cis]_0$, is given by eqn. (3),

$$\frac{[cis]_t}{[cis]_0} = \frac{1}{\pi^{1/2}} \int_{-\infty}^{+\infty} \exp(-x^2)\exp[-k_{\mathrm{AV}} t \exp(\gamma x)]\mathrm{d}x \qquad (3)$$

where x is the stochastic variable of a Gaussian distribution, k_{AV} is the mean rate constant, and γ is the spread of the Gaussian distribution of the free energy of activation. The free energy of activation is represented as $\Delta G^\ddagger=\Delta G^\ddagger_{\mathrm{AV}}-\gamma xRT$, where $\Delta G^\ddagger_{\mathrm{AV}}$ is the mean free energy of activation.

The *cis*→*trans* thermal isomerization of the 3 : 1-*m*-MTDATA film was found to fit eqn. (3) with the parameters of $k_{\mathrm{AV}}=0.034$ min^{-1} and $\gamma=1.8$. The value of k_{AV} is much larger than the first-order rate constant (0.003 min^{-1}) of the *cis*→*trans* thermal isomerization of DAAB in benzene solution. These results suggest that most *cis*-isomers photochemically generated in the 3 : 1-*m*-MTDATA film take strained conformations and their free energies are subject to the Gaussian distribution.

In the case of the 100 : 1-*m*-MTDATA film, the *cis*→*trans* thermal isomerization of DAAB could not be analyzed by the Gaussian Model but instead could be analyzed by first-order kinetics for a two component system [eqn. (4)],

$$\frac{[cis]_t}{[cis]_0} = f_1 \exp(-k_1 t) + f_2 \exp(-k_2 t) \qquad (4)$$

where f_i and k_i are the fractions and the rate constants for the faster ($i=1$) and the slower ($i=2$) components, respectively. Likewise, the *cis*→*trans* thermal isomerization of DAAB in the polystyrene film was analyzed by first-order kinetics for a two component system. Table 3 lists the kinetic parameters for the reactions in the 100 : 1-*m*-MTDATA film, the polystyrene film, and the benzene solution at 30 °C. The rate constant of the faster component for the 100 : 1-*m*-MTDATA film and the polystyrene film was found to be *ca.* 27 and *ca.* 21 times as large as that of the slower component. The rate constant of the slower component for the 100 : 1-*m*-MTDATA and polystyrene films was found to be the same as for solution. It is suggested that the faster and the slower components are attributed to the reactions of the strained *cis*-isomer and the structurally relaxed one, respectively. It is noteworthy that the fraction of the faster component (f_1) is considerably larger for the 100 : 1-*m*-MTDATA film ($f_1=0.54$) than for the polystyrene matrix film ($f_1=0.12$). This leads to a larger apparent rate constant at the initial stage for the 100 : 1-*m*-MTDATA film than for the polystyrene film. These results indicate that the ratio of the number of the strained *cis*-isomers to the relaxed *cis*-isomers at the photostationary state is much larger for the 100 : 1-*m*-MTDATA film than for the polystyrene film. The reason why the *cis*→*trans* thermal isomerization of DAAB both in the 100 : 1-*m*-MTDATA film and in the polystyrene film can be analyzed in terms of the first-order kinetics for a two component system rather than the Gaussian model is that both the 100 : 1-*m*-MTDATA film and the polystyrene film involve the reaction of the relaxed *cis*-isomer to the extent of 46% and 88%, respectively.

Table 3 Kinetic parameters based on eqn. (4) 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 larger apparent rate constant for the *cis*→*trans* thermal isomerization in the *m*-MTDATA film relative to the polystyrene film also suggests that the average size of the local free volume in the *m*-MTDATA glass is smaller than that in the polystyrene glass.

The results of a larger *cis*-fraction at the photostationary state and a larger ratio of the strained *cis*-isomer to the relaxed one for the 3 : 1-*m*-MTDATA film relative to the 100 : 1-*m*-MTDATA film are ascribed to the difference in the size and distribution of the local free volume between the 3 : 1-*m*-MTDATA and 100 : 1-*m*-MTDATA films. It is thought that *trans*-DAAB can be isomerized to *cis*-DAAB when the local free volume around the molecule is larger than V_0; however, photogenerated *cis*-DAAB is trapped in a strained conformation in the host matrix when the local free volume is smaller than V_1. The comparison of the *cis*-isomer fraction (Y) at the photostationary state and the ratio of the strained *cis*-isomer to the relaxed one between the 3 : 1- and 100 : 1-*m*-MTDATA films suggests that the fraction of the free volume larger than V_0 is larger for the 3 : 1-*m*-MTDATA film than for the 100 : 1-*m*-MTDATA film, but that the size of the local free volume is smaller than V_1 for the 3 : 1-*m*-MTDATA film, whereas a local free volume larger than V_1 is available for the 100 : 1-*m*-MTDATA film.

Temperature dependence of the kinetic parameters for the 100 : 1-*m*-MTDATA film

The temperature dependence of the kinetic parameters for the *cis*→*trans* thermal isomerization were investigated with regard to the 100 : 1-*m*-MTDATA film, the reaction of which was analyzed by first-order kinetics for a two component system according to eqn. (4). Fig. 5 shows the first-order plots for the *cis*→*trans* thermal isomerization of the 100 : 1-*m*-MTDATA film at various temperatures below T_g. The apparent rate constant of the reaction increased with rising temperature. The kinetic parameters in eqn. (4) obtained for the 100 : 1-*m*-MTDATA film are summarized in Table 4. The results show that the values of f_1 and f_2 are almost constant irrespective of

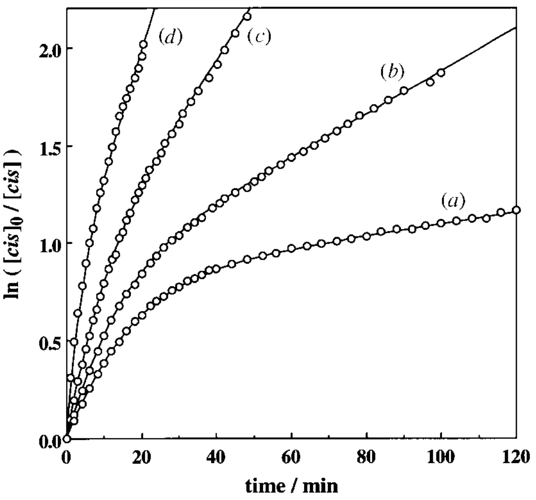


Fig. 5 First-order plots for the *cis→trans* thermal isomerization of DAAB in 100 : 1-*m*-MTDATA film at various temperatures: (*a*) 30, (*b*) 40, (*c*) 50 and (*d*) 60 °C. Solid lines are fitting curves based on eqn. (4).

Table 4 Kinetic parameters based on eqn. (4) for the *cis→trans* thermal isomerization of DAAB in 100 : 1-*m*-MTDATA film at various temperatures

$T/°C$	k_1/min^{-1}	f_1	k_2/min^{-1}	f_2
30	0.083	0.54	0.003	0.46
40	0.11	0.54	0.011	0.46
50	0.16	0.54	0.029	0.46
60	0.37	0.53	0.061	0.47
75[a]	—	—	0.346	1.00
77[a]	—	—	0.382	1.00

[a]Single component.

the temperature, whereas the rate constants k_1 and k_2 increase with rising temperature. Fig. 6 shows the Arrhenius plots for both k_1 and k_2. The activation energies for the reactions of the faster and the slower components were determined to be 41 and 84 kJ mol^{-1}, respectively. The activation energy for the slower reaction component is similar to that for solution (*ca.* 88 kJ mol^{-1}),[41,42] but the activation energy for the faster reaction component is almost half of that of the slower reaction component. It is thought that the slower and the faster reactions are attributed to the *cis→trans* thermal isomerization reactions from the relaxed *cis*-isomer and from the *cis*-isomer trapped in strained conformations in the *m*-MTDATA host matrix, respectively. On the other hand, the *cis→trans* thermal isomerization of the 100 : 1-*m*-MTDATA supercooled liquid film in the temperature region above T_g, at 75 and 77 °C, was found to follow simple first-order kinetics, as shown in Table 4 and Fig. 6.[43] The rate constant is comparable to that predicted from the Arrhenius plots for the slower reaction component below T_g. This result suggests that the photogenerated *cis*-isomer can take a relaxed conformation in the supercooled liquid state, probably because molecular motion is not restricted in the supercooled liquid state.

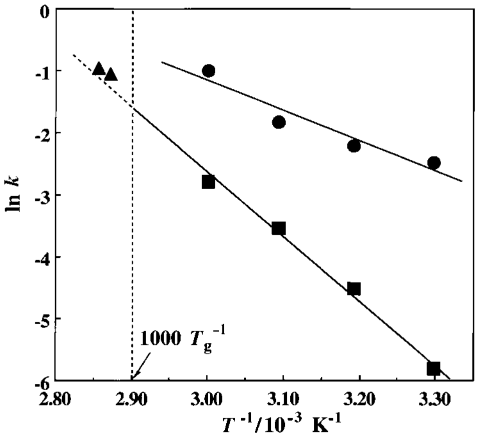


Fig. 6 Arrhenius plots for the *cis→trans* thermal isomerization reaction of 100 : 1-*m*-MTDATA film: (●) faster reaction component below T_g, (■) slower reaction component below T_g, and (▲) above T_g.

Summary

The photochromic behavior of DAAB dispersed in a molecular glass of *m*-MTDATA was investigated in order to elucidate the properties of the molecular glass as a novel host matrix and to gain information on the microstructure of the molecular glass. The *m*-MTDATA glass was found to function as a host matrix, homogeneously embedding the photochromic molecule DAAB. It was 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 *cis→trans* thermal isomerization of DAAB in the *m*-MTDATA glass matrix is considerably larger than those in a polystyrene matrix and in a benzene solution. These results indicate that there is a large difference in the size and distribution of local free volume between the molecular glass of *m*-MTDATA and the polystyrene matrix. That is, the local free volume in the molecular glass of *m*-MTDATA is suggested to be smaller than that in the polystyrene glass. The present study presents the first example of photochromic behavior in a molecular glass as a novel host matrix and can be extended to other photochromic compounds and other molecular glasses to gain further information on the properties of molecular glasses as a novel class of host matrix and on the microstructure of molecular glasses.

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43 The reaction in the higher temperature region above 77 °C could not be carried out due to crystallization of the reaction system.

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