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Marked Difference in the Reaction Rate of an Azobenzene-based Photochromic Amorphous Molecular Material between Films Prepared by Vacuum Deposition and Spin Coating

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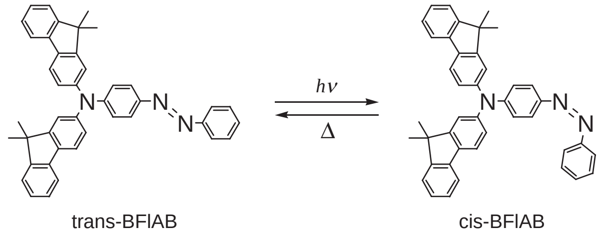
A marked difference in the reaction rate of an azobenzene-based photochromic amorphous molecular material between films prepared by vacuum deposition and spin coating was found, the rate for the vacuum-deposited film being significantly faster compared to spin-coated amorphous film; this result indicates that the microstructures of amorphous films prepared by the above two methods are different from each other, suggesting that the local free volume of the vacuum-deposited film is smaller than that of the spin-coated film.

Control over materials morphology is a key issue in materials science and practical applications. Small organic molecules that readily form stable amorphous glasses, namely, amorphous molecular materials, have recently received a great deal of attention as a new class of functional materials for various applications.[1–3] We have proposed a new concept of photochromic amorphous molecular materials, created such materials, and investigated their reactions.[4–9] With regard to azobenzene-based photochromic amorphous molecular materials, photoinduced surface relief grating formation[7–11] and nonlinear optical properties[12] have been studied.

Amorphous molecular materials are capable of forming uniform amorphous films by vacuum deposition and spin coating from solution.[1] It is of great interest and significance from both fundamental science and technological applications to investigate how the microstructures, reaction behavior, and properties of amorphous films differ depending on film preparation methods, e.g., vacuum deposition and spin coating from solution. We report here a marked difference in reaction behavior between amorphous films prepared by the vacuum deposition and spin-coating methods. The present study is concerned with the cis–trans thermal isomerization of the photogenerated cis form of an azobenzene-based photochromic amorphous molecular material, 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFlAB, $Tg = 97\,°\mathrm{C}$) (Scheme 1).



Scheme 1.

Vacuum-deposited BFlAB film was prepared by vacuum deposition onto a glass substrate at a deposition rate of $0.3\,\mathrm{nm\,s^{-1}}$ at 2×10^{-5} Torr. Spin-coated BFlAB film was prepared by spin coating (2000 rpm) from its benzene solution (ca. $2 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) onto a glass substrate and dried under reduced pressure (ca. 2 Torr) at 60 °C for 1 h. The film thicknesses were ca. 50–60 nm.

Both vacuum-deposited and spin-coated films exhibited photochromism resulting from the trans–cis and cis–trans photoisomerizations and the cis–trans thermal isomerization. When the film was irradiated with 450 nm-light at ca. $2\,\mathrm{mW\,cm^{-2}}$ from a 500 W Xenon lamp (UXL-500D, USHIO) through an interference filter (IF-S 450, Vacuum Optics Co.) using an optical fiber, the absorbance at around 460 nm gradually decreased and reached the photostationary state in ca. 150 s, no further spectral change taking place. When photoirradiation was stopped, the absorbance at around 460 nm gradually increased due to the backward cis–trans thermal isomerization.

We have previously shown that the backward cis–trans thermal isomerization rate of the photogenerated cis isomer of BFlAB as spin-coated amorphous film is accelerated relative to solution[8] and that such acceleration effect becomes more prominent as the irradiation time for generating the cis isomer becomes shorter.[13]

In the present study, it was found that the rate of the thermal isomerization from the photogenerated cis form to the trans form as amorphous film greatly differ depending upon the film preparation methods, i.e., vacuum deposition and spin coating from solution. Figure 1 shows the first-order plots, i.e., plots of $-\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs t, for the cis–trans thermal iso-

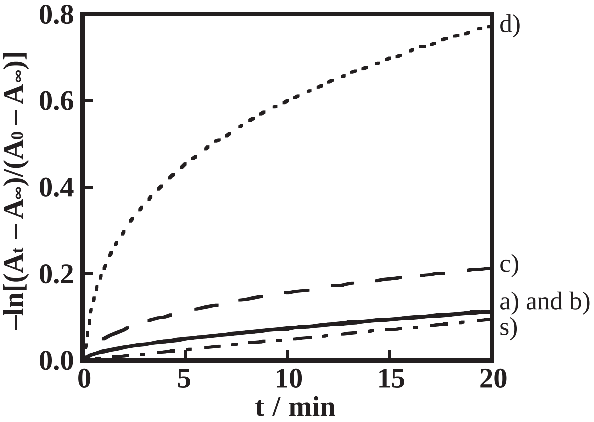


Figure 1. First-order plots for the cis–trans thermal isomerization of BFlAB after irradiation with 450 nm-light. a), c) Spin-coated film. b), d) Vacuum-deposited film. s) Toluene solution. Irradiation time: a), b) 150 s (photostationary state), c), d) 5 s. Plots a) and b) are almost overlapped.

merization of photogenerated BFlAB as amorphous film at 30 °C, where A_t denotes the absorbances of the film at 460 nm at time t after photoirradiation was stopped. The plot for the reaction in solution is also included in the figure for comparison. The first-order plots for the reaction as film after the reaction system had reached the photostationary state by photoirradiation for over 150 s, where the cis fraction was 0.50, were the same irrespective of the film preparation methods, vacuum deposition and spin coating (Figures 1a and 1b), the rates as film being accelerated relative to solution (Figure 1s). On the other hand, when photoirradiation was stopped before the reaction system reached the photostationary state, much pronounced rate acceleration was observed for the vacuum-deposited film compared to the spin-coated film. That is, when the film as-prepared, which consists of all the trans isomers, was photoirradiated for 5 s (the cis fractions were ca. 0.12 and 0.15 for the vacuum-deposited and spin-coated films, respectively), the rate of the cis–trans thermal isomerization as the vacuum-deposited film was much faster (Figure 1d) than that as the spin-coated film (Figure 1c). While the conversion of the photogenerated cis form to the trans form was ca. 20% in 20 min for the spin-coated film, that was ca. 55% for the vacuum-deposited film, the conversion for the vacuum-deposited film being 2.8 times larger than that for the spin-coated film. Annealing of the spin-coated film at 120 °C for 10 min also showed rate acceleration (cis to trans conversion in 20 min: ca. 22%), but it was considerably smaller as compared with the rate acceleration observed for the vacuum deposited film.

The cis–trans thermal isomerization reaction as the spin-coated film was analyzed in terms of the first-order kinetics of the two components according to eq. 1;

$$(A_t - A_\infty)/(A_0 - A_\infty) = \mathrm{f}_1 \exp(-k_1 t) + \mathrm{f}_2 \exp(-k_2 t) \quad (1)$$

where f_1 and f_2 are the fractions of the fast and slow rate components, and k_1 and k_2 are the rate constants for the fast and slow components, respectively. The result showed that the fraction of the fast rate component (f_1) was 0.05 at the photostationary state, increasing to 0.12 when the photoirradiation time was 5 s.[13] It is understood that the photogenerated cis isomer molecules as film are partly trapped in constrained conformations, which go back faster to the trans isomer molecules than the structurally relaxed cis isomer molecules and that the fraction of the cis isomers trapped in constrained conformations is greater when the photoirradiation time becomes shorter, gradually decreasing to give a constant value at the photostationary state. It is thought that the local free volume is enlarged by repeated trans–cis and cis–trans photoisomerizations during the time for the reaction system to reach the photostationary state.

The reaction as the vacuum-deposited film after the reaction system had reached the photostationary state could also be analyzed by eq. 1. It was found that the kinetic parameters for the reaction as the vacuum-deposited film were almost the same as those for the reaction as the spin-coated film (Table 1). However, when the reaction system was irradiated for a much shorter time of 5 s, the reaction as the vacuum-deposited film could not be approximated in terms of the two components in eq. 1. The much faster rate for the vacuum-deposited film than the spin-coated film suggests that the fractions of the cis isomers trapped in constrained conformations with different rate constants as the vacuum-deposited film is much greater than that as the spin-coated film.

Table 1. Kinetic parameters based on eq. 1 for the cis–trans thermal isomerization of BFlAB as amorphous film

preparation method	irradiation time	f_1	k_1/min^{-1}	f_2	k_2/min^{-1}
spin coating	5 s	0.12	0.27	0.88	4.0×10^{-3}
spin coating	150 s	0.05	0.23	0.95	3.2×10^{-3}
vacuum deposition	5 s	—[a]	—[a]	—[a]	—[a]
vacuum deposition	150 s	0.05	0.24	0.95	3.2×10^{-3}

[a] The analysis in terms of eq. 1 was not successful.

Since the fraction of the photogenerated cis isomer is small when the film is irradiated for the short time of 5 s, the backward thermal cis–trans isomerization reaction as film is thought to reflect the microstructures of as-prepared films. The significantly larger rate acceleration observed for the vacuum-deposited film than the spin-coated film suggests that the local free volume of the vacuum-deposited film as-prepared is smaller than that for the spin-coated film as-prepared. In addition, the result that the first-order plots for both the vacuum-deposited and spin-coated films which reached the photostationary state were the same indicates that the local free volume of both the vacuum-deposited and spin-coated films is gradually enlarged during repeated photoisomerizations, resulting in the same size when the systems reached the photostationary state.

In summary, a significant effect of the preparation methods of amorphous film, vacuum deposition and spin coating from solution, on the cis–trans thermal isomerization rate was observed when photoirradiation time was short. To our knowledge, this is the first example that demonstrates a marked difference in the reaction behavior between the amorphous films prepared by the vacuum deposition and spin-coating methods. It is indicated that the microstructures of amorphous films prepared by vacuum deposition and spin coating from solution are different from each other.

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