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4-[Di(biphenyl-4-yl)amino]azobenzene and 4,4′-bis[bis(4′-*tert*-butylbiphenyl-4-yl)amino]azobenzene as a novel family of photochromic amorphous molecular materials

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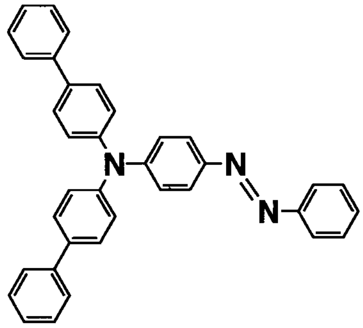
We have created photochromic amorphous molecular materials containing an azobenzene chromophore, 4-[di(biphenyl-4-yl)amino]azobenzene and 4,4′-bis[bis(4′-*tert*-butylbiphenyl-4-yl)amino]azobenzene (*t*-BuBBAB), which readily form amorphous glasses above room temperature and exhibit photochromism in their amorphous films. We have shown that the photogenerated *cis*-form in the amorphous film can be stabilized at ambient temperature by the incorporation of a bulky group; the backward *cis*→*trans* thermal isomerization can be controlled by temperature for *t*-BuBBAB.

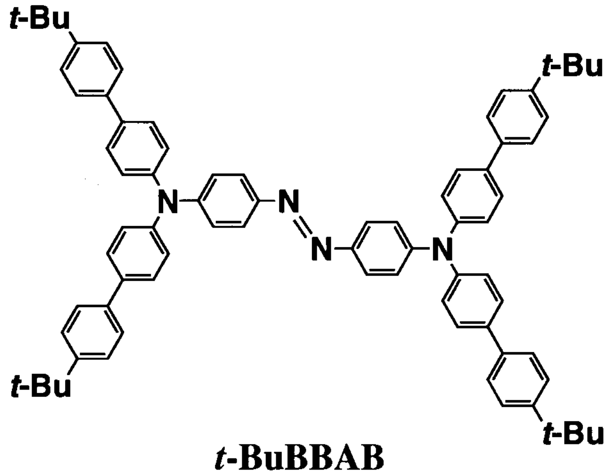
Photochromic materials have recently been attracting a great deal of attention because of their potential technological applications to optical recording for storage of information, optical switching, *etc.* In applying photochromic materials to practical applications, they may be used in the form of a solid film. Thus, photochromism in the solid state has been a subject of current interest. Extensive studies have been made of photochromism of polymers containing photochromic chromophores and composite polymer systems, where low molecular-weight photochromic compounds are dispersed in polymer binders.[1–8]

It is of interest and significance to create low molecular-weight organic photochromic compounds that readily form stable amorphous glasses above room temperature, which we refer to as ‘photochromic amorphous molecular materials’ or ‘photochromic molecular glasses’. Photochromic amorphous molecular materials may constitute a novel class of photochromic materials that exhibit glass-transition phenomena usually associated with polymers. They form uniform amorphous films by themselves and have the advantage that there is no dilution of photochromic chromophores relative to photochromic polymers and composite polymer systems, where low molecular-weight photochromic compounds may crystallize at high concentrations. However, very few studies have been made of photochromic amorphous molecular materials because low molecular-weight organic compounds generally tend to crystallize readily. Spirooxazine photochromic compounds have recently been reported to form amorphous glasses with glass-transition temperatures (T_gs) between −45 and 29 °C.[9]

We have been studying the creation of amorphous molecular materials.[10] In the present study, we have designed and synthesized novel photochromic compounds containing an azobenzene chromophore, 4-[di(biphenyl-4-yl)amino]azobenzene (DBAB) and 4,4′-bis[bis(4′-*tert*-butylbiphenyl-4-yl)amino]azobenzene (*t*-BuBBAB), for making photochromic amorphous molecular materials. These compounds were found to form readily stable amorphous glasses with T_gs of 68 and 177 °C, respectively, and to exhibit photochromism in their amorphous films. It is also shown that the photogenerated *cis*-isomer in the amorphous film can be stabilized at ambient temperature by the incorporation of a bulky substituent and hence, the backward *cis*→*trans* thermal isomerization can be controlled by temperature for *t*-BuBBAB.



DBAB



***t*-BuBBAB**

DBAB was synthesized by the reaction of 4-aminoazobenzene (3.0 g) with 4-iodobiphenyl (20 g) in the presence of copper powder (0.8 g) and potassium hydroxide (7.0 g) in decalin (10 ml) at 150 °C for 8 h. *t*-BuBBAB was synthesized by refluxing a THF solution (40 ml) of *N,N*-bis(4′-*tert*-butylbiphenyl-4-yl)-4-nitroaniline (100 mg) in the presence of $LiAlH_4$ (68 mg) for 2 h. *N,N*-Bis(4′-*tert*-butylbiphenyl-4-yl)-4-nitroaniline was prepared by the reaction of *p*-nitroaniline (0.72 g) with 4-*tert*-butyl-4′-iodobiphenyl (7.0 g) in the presence of copper powder (2.0 g), potassium carbonate (8.6 g), and 18-crown-6 (1.5 g) in 1,2,4-trichlorobenzene (10 ml) at 165 °C for 6 h. These new compounds were identified by various spectroscopic techniques, mass spectrometry, and elemental analysis.[11]

Both DBAB and *t*-BuBBAB were found to readily form

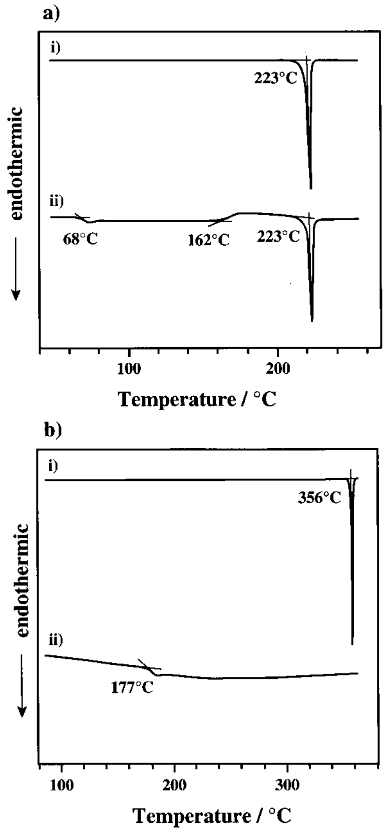


Fig. 1 DSC curves of a) DBAB and b) *t*-BuBBAB. i) Polycrystalline samples obtained by recrystallization from acetonitrile (DBAB) and from the mixed solvent of benzene and hexane (*t*-BuBBAB). ii) The glass samples obtained by cooling the melt.

amorphous glasses when the melt samples were cooled on standing in air, as evidenced by differential scanning calorimetry (DSC), X-ray diffraction, and polarizing microscopy. Fig. 1 shows DSC curves of DBAB and *t*-BuBBAB. When the crystalline samples of DBAB and *t*-BuBBAB were heated, an endothermic peak due to melting was observed at 223 and 356 °C, respectively. When the melt samples were cooled on standing in air, amorphous glasses were obtained *via* the supercooled liquid state. When the glass samples of DBAB and *t*-BuBBAB were again heated, the glass-transition phenomenon was observed at 68 and 177 °C, respectively. On further heating, crystallization took place around 162 °C, followed by melting at 223 °C for DBAB, but no crystallization phenomenon was observed for the *t*-BuBBAB glass.

The amorphous film of DBAB (thickness: 0.10 mm, 1.6×10^{-5} mol cm^{-2}) was prepared by vacuum deposition at a rate of 2–3 Å s^{-1} at *ca.* 10^{-5} Torr. As Fig. 2 shows, irradiation of the film with 450 nm light (0.44 mW cm^{-2}) at room temperature caused a decrease in the absorbance around 450 nm due to the photoisomerization of *trans*-DBAB to the *cis*-form. The *cis*-fraction of DBAB in the amorphous film at the photostationary state attained by irradiation for *ca.* 15 min at 30 °C was 0.53; this value is smaller than that (0.81) for the toluene solution. It is suggested that the local free volume around the remaining *trans*-DBAB molecules in the amorphous film is not large enough to allow the isomerization from the *trans*- to the *cis*-form to the extent observed for the solution. When irradiation was stopped after the reaction system had reached the photostationary state, the electronic absorption spectrum of the film gradually recovered to the original one in *ca.* 24 h at room temperature due to the backward *cis*→*trans* thermal isomerization of DBAB (Fig. 3a).[12]

In applying photochromic amorphous molecular materials to the rewritable information storage system, the photogenerated molecule should be stable at ambient temperature. Generally, the *cis*-form of azobenzene derivatives goes back to the *trans*-form at ambient temperature in the dark. The rate constants for the backward *cis*→*trans* thermal isomerization of polymers containing the pendant azobenzene moiety and low molecular-weight azobenzene derivatives dispersed in polymer binders have been reported to be in the range from 10^{-3} to 10^{-2} min^{-1} at room temperature.[3,5] A polyurethane containing the azobenzene chromophore in the main chain has been reported to undergo backward *cis*→*trans* thermal isomerization with a slower rate constant of 1.7×10^{-4} min^{-1} at 3 °C.[4]

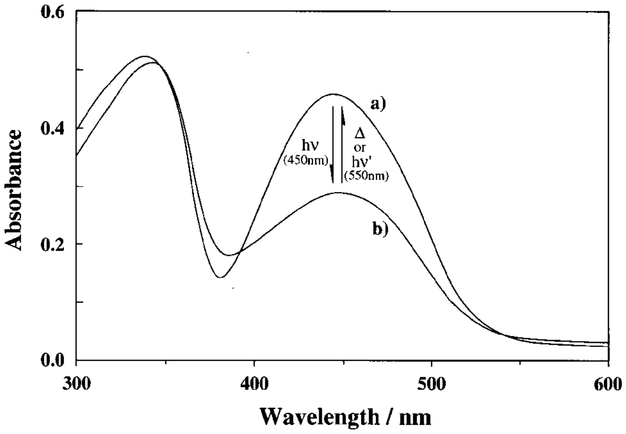


Fig. 2 The electronic absorption spectral change of a DBAB amorphous film: a) before irradiation, b) photostationary state upon irradiation with 450 nm light from a 500 W Xenon lamp (UXL-500D, USHIO) through an interference filter (IF-S 450, Vacuum Optics Co.).

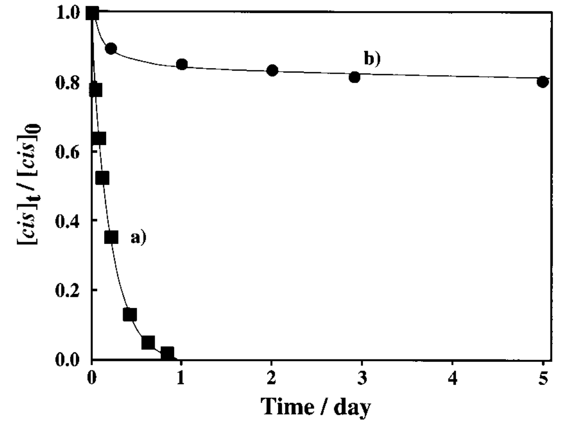


Fig. 3 Thermal decay of a) *cis*-DBAB and b) *cis*-*t*-BuBBAB at 30 °C in the amorphous film.

It was expected that the introduction of a bulky group may stabilize the photogenerated *cis*-form. Based on this idea, we have designed and synthesized *t*-BuBBAB. The *t*-BuBBAB amorphous film (thickness: 0.05 mm, 5×10^{-6} mol cm^{-2}), which was prepared by spin-coating from a benzene solution (*ca.* 3×10^{-2} mol dm^{-3}), underwent *trans*→*cis* photoisomerization on irradiation with 500 nm light (4.6 mW cm^{-2}). The *cis*-fraction of *t*-BuBBAB at the photostationary state attained by irradiation for *ca.* 1 h was 0.15, being smaller than that for the toluene solution (0.71). The *cis*-form of *t*-BuBBAB photogenerated in the amorphous film was found to be fairly stable; 80% of the photogenerated *cis*-*t*-BuBBAB still remained after 5 days at room temperature (rate constant: less than 10^{-5} min^{-1} after slight decay at the initial time) (Fig. 3b). As far as we know, this is the most stable example of a *cis*-azobenzene derivative photogenerated in the amorphous film. It is thought that most photogenerated *cis*-*t*-BuBBAB molecules have lost the space needed to isomerize to the *trans*-form in the film because of the changes in the surrounding environment due to the motion of the bulky group in the process of *trans*→*cis* photoisomerization. When the film was heated up to 140 °C, however, the photogenerated *cis*-*t*-BuBBAB was transformed into the *trans*-*t*-BuBBAB within *ca.* 10 min. Thus, the backward *cis*→*trans* thermal isomerization can be controlled by temperature.

In summary, novel photochromic amorphous molecular materials containing an azobenzene chromophore, DBAB and *t*-BuBBAB, have been created. They undergo reversible *trans*→*cis* and *cis*→*trans* isomerizations in their amorphous films. The stabilization of the photogenerated *cis*-form and the control of the backward *cis*→*trans* thermal isomerization by temperature are achieved by introducing a bulky substituent.

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11 DBAB: Yield 45%. Mp 223 °C; δ_H (600 MHz, THF-d_8, TMS) 7.20 (d, 2H), 7.27 (d, 4H), 7.28 (t, 2H), 7.40 (t, 4H), 7.41 (t, 1H), 7.47 (t, 2H), 7.63 (d, 8H), 7.84 (d, 2H), 7.86 (d, 2H); *m*/*z* (EI) 501 (M^+); Calc. for $C_{36}H_{27}N_3$: C, 86.20; H, 5.42; N, 8.38. Found: C, 86.04; H, 5.41; N, 8.23%; λ_{max}(toluene) (log ε) for *trans*-DBAB: 335 nm (4.5), 435 nm (4.5); λ_{max}(toluene) (log ε) for *cis*-DBAB: 343 nm (4.5), 451 nm (3.9).

t-BuBBAB: Yield 21%. Mp 356 °C; δ_H (600 MHz, 1,4-dioxane-d_8, TMS) 1.34 (s, 36H), 7.23 (d, 4H), 7.28 (d, 8H), 7.46 (d, 8H), 7.54 (d, 8H), 7.57 (d, 8H), 7.80 (d, 4H); *m*/*z* (EI) 1044 (M^+); Calc. for $C_{76}H_{76}N_4$: C, 87.31; H, 7.33; N, 5.36. Found: C, 87.11; H, 7.24; N, 5.35%; λ_{max}(toluene) (log ε) for *trans*-*t*-BuBBAB: 345 nm (4.7), 480 nm (4.7); λ_{max}(toluene) (log ε) for *cis*-*t*-BuBBAB: 342 nm (4.8), 488 nm (3.9).

12 The *cis*→*trans* thermal isomerization in the amorphous film could be analyzed in terms of the first-order kinetics consisting of two components. The rate constants for the faster component with a fraction of 0.05 and slower one with a fraction of 0.95 were 0.12 min^{-1} and 3.3×10^{-3} min^{-1}, respectively.

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