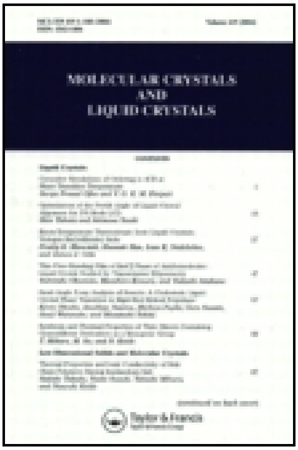

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Photochromic Amorphous Molecular Material: Polarized-Light Induced Dichroism of Amorphous Film of 4-[Bis(9,9-dimethylfluoren-2-yl)amino]azobenzene

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Dichroism of amorphous film of an azobenzene-based photochromic amorphous molecular material, 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFlAB), induced by irradiation with linearly polarized Ar^+ *laser light has been investigated.*

Keywords: azobenzene; dichroism; photochromism; photochromic amorphous molecular material

INTRODUCTION

Photochromic materials have recently attracted renewed attention from the viewpoints of both academic interest and technological applications [1]. Photoinduced dichroism of photochromic compounds in solid and liquid crystalline states is one of the subjects of interest. Two types of polarized-light induced dichroism and birefringence are known. One is due to the change in molecular alignment by polarized-light irradiation, which is known as "the Weigert effect" [2]. Utilizing this effect, modulation of the molecular alignment of azobenzene-containing polymer liquid crystals [3–6] and liquid crystals on the monolayer of an azobenzene-containing molecule [7] has been performed. The other type is due to the bleaching of photochromic molecules lying in a specific

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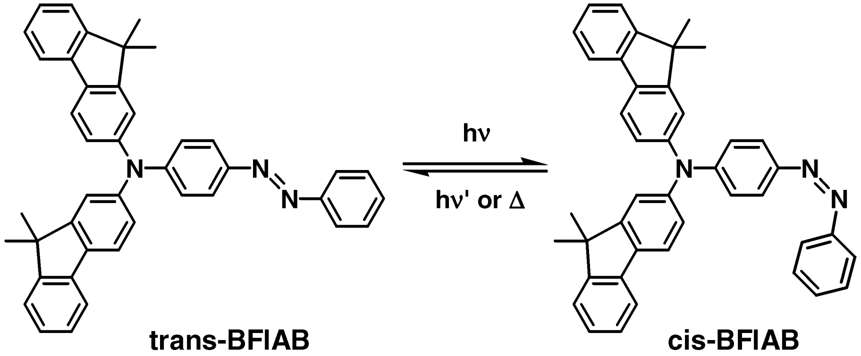
direction in isotropic solids by irradiation with linearly polarized light. This type of polarized-light induced dichroism has been demonstrated for fulgide-doped poly(methyl methacrylate) [8,9] and a sol-gel glass containing a dithienylethene moiety [10].

As a part of our studies on amorphous molecular materials [11], we have proposed a new concept, "photochromic amorphous molecular materials" [12] and have created two families of photochromic amorphous molecular materials based on azobenzene [12–15] and dithienylethene [16–18]. We have demonstrated that dichroism of the amorphous films of dithienylethene-based photochromic amorphous molecular materials is induced by irradiation with linearly polarized light; this dichroism results from the bleaching of photocyclized colored molecules lying in a specific direction [17,18]. Dual image formation at the same location was realized by the use of this type of polarized-light induced dichroism [17,18].

In the present study, polarized-light induced dichroism of an amorphous film of an azobenzene-based photochromic amorphous molecular material, 4-[bis(9,9-dimetnylfluoren-2-yl)amino]azobenzene (BFlAB), was investigated.



EXPERIMENTAL

Preparation of BFlAB Amorphous Film

BFlAB was synthesized according to our previous paper [13]. An amorphous film of BFlAB was prepared on a transparent glass substrate by spin coating from benzene solution (ca. 5×10^{-2} mol dm^{-3}). The film was dried at 120°C for more than 1 h under reduced pressure before experiments.

Measurement of Polarized-Light Induced Dichroism

Amorphous film of BFlAB was irradiated with linearly and circularly polarized Ar^+ laser light (488 nm; ca. 2 mWcm^{-2}) through a polarizer. Circularly polarized light was obtained with a $\lambda/4$ wave plate. Dichroism was monitored by the polarized absorption spectra of the film, as measured by a Hitachi U-3500 spectrophotometer with a polarizer. Polarized absorption spectra were measured before and after irradiation. From the spectra it was confirmed that the BF1AB amorphous film before photoirradiation was isotropic. Since it was difficult to measure polarized absorption spectra immediately after irradiation was stopped, the spectra were recorded 3 minutes after cessation of irradiation. Before measurement of the spectra, ca. $3\sim4\%$ of the photogenerated cis-isomers had been transformed into the trans-isomers by the backward cis-trans isomerization. Polarized absorption spectra were also measured after the irradiated film was annealed for 48 h at 50°C.

RESULTS AND DISCUSSION

Spin-coated amorphous film of BFlAB was irradiated with linearly polarized Ar^+ laser light for 60 min at room temperature. Figure 1 shows the polarized absorption spectra of the film before and after

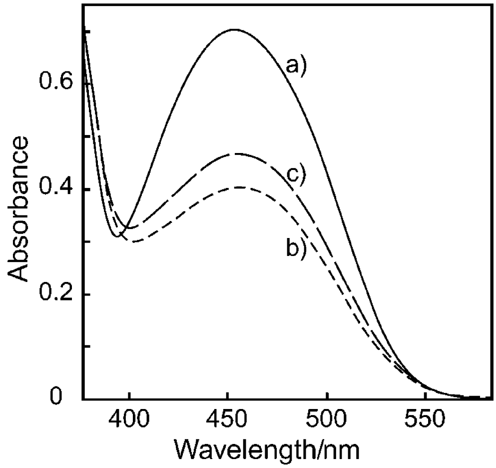


FIGURE 1 Electronic absorption spectra of BFlAB amorphous film a) before photoirradiation and b,c) after irradiation with linearly polarized light (488 nm). b) $\theta=0°$, c) $\theta=90°$.

irradiation with the laser light. The absorbance of the film at ca. 460 nm decreased upon irradiation because of the trans-cis photoisomerization of BFlAB. It was found that the absorbance of the irradiated film at ca. 460 nm was greater for $\theta = 90^\circ$ than for $\theta = 0^\circ$, where θ is the angle between the polarization directions of the irradiated and probe light. It is understood that this dichroism was mainly caused by the bleaching of the trans-isomer molecules lying in a specific direction in the isotropic amorphous film by irradiation with linearly polarized light. That is, when the amorphous film with random orientation of trans-isomer molecules is irradiated with linearly polarized light, the molecules with a long axis of the azobenzene chromophore being parallel to the polarization direction of the irradiated linearly polarized light absorb the light more effectively to be transformed into the cis-isomers. Thus, the number of trans-isomers remaining unfaded becomes larger with increasing θ. Such dichroism was not induced by irradiation with circularly polarized Ar^+ laser light.

Figure 2 shows the polarized absorption spectra of the film after irradiation with linearly polarized laser light for 60 min, followed by annealing for 48 h at 50°C so that the most photogenerated cis-isomers are thermally transformed into trans-isomers. It was found that the absorbance of the annealed film at ca. 460 nm was greater for $\theta = 90^\circ$ than for $\theta = 0^\circ$. The difference between the spectra for $\theta = 0^\circ$ than for

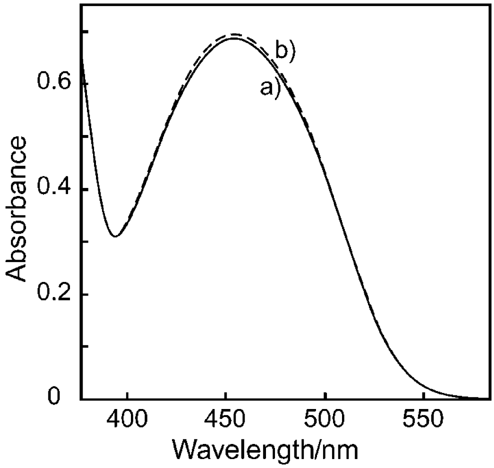


FIGURE 2 Electronic absorption spectra of BFlAB amorphous film obtained by irradiation with a linearly polarized light followed by annealing at 50°C for 48 h. a) $\theta = 0^\circ$, b) $\theta = 90^\circ$.

$\theta = 90^\circ$ is small but was reproducibly observed. The small, but definite difference between the two spectra is further supported by the following results. When the sample was heated up to 120°C, the absorption spectrum for $\theta = 0^\circ$ became identical with that for $\theta = 90^\circ$. The polarized absorption spectra for $\theta = 0^\circ$ and $\theta = 90^\circ$ were completely identical with each other for the film irradiated with circularly polarized light instead of linearly polarized light, followed by annealing.

The dichroism observed for the BFlAB amorphous film obtained by irradiation with linearly polarized light, followed by annealing, is suggested to be due to the Weigert effect. That is, when the film was irradiated with linearly polarized light, the molecules tend to rearrange their orientations during the trans-cis and cis-trans photoisomerizations so that the long axis of the azobenzene chromophore becomes perpendicular to the polarization direction of irradiated light. When the film was heated up to 120°C exceeding the Tg, the orientation of the molecules was randomized by thermal motions to give an isotropic film. The order parameter (S) of the dichroism for the BFlAB film induced by irradiation with linearly polarized light, followed by annealing, was estimated to be 0.004, which was much smaller than those observed for polymer liquid crystals, e.g., poly{6-[4-(4-ethylphenylazo)phenoxy]hexyl methacrylate} (S = 0.36) [6]. Since liquid crystalline molecules tend to spontaneously align side by side, the Weigert effect is expected to be enhanced for azobenzene-containing liquid crystalline polymers. On the other hand, BFlAB molecules do not have such tendency. Randomization of molecular alignments by the stirring effect caused by the trans-cis and cis-trans isomerizations overcome the Weigert effect. It is also possible that local free volume is not enough large for the molecules to change their orientations in amorphous film.

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