Synthesis and Photoinduced Surface Relief Grating Formation of a Novel Azobenzene-based Photochromic Amorphous Molecular Material, 4-[Bis(9,9-dimethylfluoren-2-yl)amino]-4'-nitroazobenzene

Hideyuki Nakano*, Toru Takahashi*, Takahiro Tanino* and Yasuhiko Shirota*†

* Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871, Japan
† Department of Environmental and Biotechnological Frontier Engineering, Fukui University of Technology, 3-6-1, Gakuen, Fukui City, Fukui 910-8505, Japan

Keywords: photochromic amorphous molecular material, azobenzene, photochromism, photoinduced surface relief grating formation

1. Introduction

Recently, surface relief grating (SRG) formation by irradiation of amorphous films of azobenzene-containing polymers with two coherent laser beams has received a great deal of attention in view of both academic interest and potential technological applications for erasable and rewritable holographic memory, waveguide coupler and so on [1-6]. SRG formation takes place by mass transport induced by trans-cis photoisomerization of azobenzene chromophores. Although a few models for photoinduced SRG formation have been proposed [3,5,6], detailed mechanisms have not yet been elucidated.

As a part of our studies on amorphous molecular materials [7,8], we have proposed a new concept, "photochromic amorphous molecular materials", which constitute a new class of photochromic materials that form uniform amorphous films by themselves without polymer binders. We have designed and synthesized novel families of photochromic amorphous molecular materials based on azobenzene and dithienylethene and investigated their photochromic properties as amorphous films [7-18]. In addition, we have shown that azobenzene-based photochromic amorphous molecular materials, such as 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFIAB), are the promising candidates for SRG-forming materials [13-16].

It is of importance to clarify the relationship between molecular structure and photoinduced SRG formation. In the present study, we have designed and synthesized a novel azobenzene-based photochromic amorphous molecular material, 4-[bis(9,9-dimethylfluoren-2-yl)amino]-4'-nitroazobenzene (NO2-BFIAB). In addition, SRG-forming property of NO2-BFIAB has been investigated in comparison with that of the parent compound, BFIAB.

2. Experimental

NO2-BFIAB was synthesized as follows: 4-Amino-4'-nitroazobenzene (3.7 g, 0.015 mol) and 2-iodo-9,9-dimethylfluorene (12 g, 0.037 mol)
were refluxed in the presence of copper powder (2.4 g, 0.037 mol), K₂CO₃ (6.5 g, 0.047 mol) and 18-crown-6 (0.7 g, 0.026 mol) in mesitylene (50 ml) for 4 h under nitrogen atmosphere. After the solvent was removed under reduced pressure, the residue was extracted with toluene and washed with water. The product was purified by silica-gel column chromatography using a mixed solvent of toluene and hexane as an eluent, followed by recrystallization from cyclohexane. Yield: 3.5 g (37%), m.p.: 228°C. MS: m/z 626 (M⁺). \( \lambda_{\text{max}} \) (log ε) (toluene): 346 nm (4.6), 513 nm (4.5).

\(^1\)H NMR (750 MHz, THF): δ (ppm) = 8.37 (d, 2H), 8.01 (d, 2H), 7.89 (d, 2H), 7.74 (d, 2H), 7.72 (d, 2H), 7.43 (d, 2H), 7.39 (d, 2H), 7.29 (dd, 2H), 7.26 (dd, 2H), 7.23 (d, 2H), 7.20 (dd, 2H), 1.43 (s, 12H).

\(^13\)C NMR (188 MHz, THF): δ (ppm) = 157.2, 156.4, 154.6, 153.2, 149.3, 147.9, 147.0, 139.6, 137.1, 127.9, 127.8, 126.0, 125.6, 125.5, 123.7, 123.3, 121.9, 121.8, 121.1, 120.5, 47.4, 27.2. Calcd for C₂₂H₂₃N₄O₂C: C, 80.49; H, 5.47; N, 8.94%. Found: C, 80.31; H, 5.58; N, 8.71%.

3. Results and discussion

A novel photochromic amorphous molecular material, NO₂-BF1AB, was synthesized by the Ullmann reaction of 4'-nitro-4-aminophenylazobenzene and 2-iodo-9,9-dimethylfluorene and identified by various spectroscopy, mass spectrometry and elemental analysis.

NO₂-BF1AB was found to readily form an amorphous glass when the melt sample was cooled on standing in air. The glass-transition temperature (Tg) was determined to be 117°C by differential scanning calorimetry, which was higher than that of the parent compound, BF1AB (97°C).

NO₂-BF1AB was found to exhibit photochromism as amorphous film as well as in solution. Fig. 1 shows electronic absorption spectral change of NO₂-BF1AB amorphous film. When the film was irradiated with 500 nm-light, the absorbance around 520 nm gradually decreased due to trans-cis photoisomerization. When the irradiation was stopped after the reaction system reached to photostationary state, the absorbance gradually increased due to the backward cis-trans thermal isomerization. The ratio (R) of absorbance at \( \lambda_{\text{max}} \) at photostationary state to that before photoirradiation was found to be 0.90 for the amorphous film while the R value was 0.60 for the toluene solution. We have already observed that the R values for BF1AB were 0.64 and 0.45 for amorphous film and toluene solution, respectively, upon irradiation with 450 nm-light [13,17]. These results suggested that the cis-fraction at photostationary state as amorphous film was smaller for NO₂-BF1AB than for BF1AB.

Using the novel photochromic amorphous molecular material, NO₂-BF1AB, photoinduced SRG formation was investigated. The schematic experimental setup was illustrated in Fig. 2. The amorphous film with a thickness of ca. 50 μm was irradiated with two writing beams (Ar⁺ laser: 488 nm) with polarization angles of +45° and −45° with respect to the p-polarization at 10 mW each. SRG formation was monitored by diffraction efficiency, which was defined as the intensity ratio of the first diffraction beam to the incident beam of the probe (laser diode: 830 nm).

Fig. 3 shows the growth of SRG by irradiation with the writing beams. The diffraction efficiency gradually increased with irradiation time and was finally saturated at ca. 14%. SRG formation was confirmed by atomic force microscopy (AFM) as shown in Fig. 4. Modulation depth of the resulting SRG was found to be 310-350 nm. We have already observed that the irradiation of BF1AB amorphous film with writing beams under the similar condition for 10 min provided SRG with a modulation depth of

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**Fig. 1.** Electronic absorption spectral change of NO₂-BF1AB amorphous film. a) before photoirradiation. b) photostationary state upon irradiation with 500 nm-light.

**Fig. 2.** Schematic experimental setup for photo-induced SRG formation. S: sample, D: detector, P: polarizer, M: mirror, W: wave plate, B: beam splitter.
450-490 nm [19]. Thus, introduction of a nitro group at 4'-position of BFIAB did not enhance the SRG-forming property.

We have shown that the modulation depth of the SRG becomes larger with the increasing $T_g$ of the material [13,14,19]. However, the present study showed that the modulation depth of SRG formed on NO$_2$-BFIAB was smaller than that formed on BFIAB although the $T_g$ of NO$_2$-BFIAB is higher than that of BFIAB. The result indicated that the increasing $T_g$ of the material does not always enhance the SRG-forming property of the material. It is thought that the introduction of the nitro group increases the volume needed for trans–cis isomerization reaction so that the reaction as amorphous film is more suppressed for NO$_2$-BFIAB than for BFIAB, and hence the SRG-forming property was not enhanced by introduction of nitro group into BFIAB. The results of electronic absorption spectral changes of amorphous films upon photoirradiation as described above suggested the trans–cis isomerization as amorphous film was more suppressed for NO$_2$-BFIAB than for BFIAB. The present study provided important information for molecular design of photochromic amorphous molecular materials with excellent SRG-forming properties.

References