Photoinduced Surface Relief Grating Formation Using a Photochromic Amorphous Molecular Material, \(N,N'\)-Bis(9,9-dimethylfluoren-2-yl)-4-(4-pyridylazo)aniline

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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 e.g. erasable and rewritable holographic memory [1-7]. SRG formation is believed to take place by mass transport induced by trans-cis photoisomerization of azobenzene chromophores. Although a few models for photoinduced SRG formation have been proposed [3,5-7], detailed mechanisms have not yet been elucidated.

In contrast to polymers, we have been performing studies of photoinduced SRG formation using azobenzene-based photochromic amorphous molecular materials, namely low molecular-weight photochromic materials that readily form amorphous glasses above room temperature [8-12]. For example, relatively large SRG with a modulation depth of ca. 500 nm could be inscribed on an amorphous film of 4-[bis(9,9-dimethylfluoren-2-yl)amino]azobenzene (BFIAB) [12]. In addition, we have demonstrated that photoinduced SRG formation can also take place on a single crystal of 4-(dimethylamino)azobenzene [13,14] and on a co-crystal of BFIAB and ethyl acetate [15].

It is of interest to introduce a pyridyl group as a hydrogen-accepting site for hydrogen bonding into azobenzene-based photochromic amorphous molecular materials because SRG-forming properties of amorphous films of such molecules are expected to be controllable by doping with appropriate hydrogen-donating molecules such as alcohols and acids. In the present study, a novel photochromic amorphous molecular material possessing pyridyl group, \(N,N'\)-bis(9,9-dimethylfluoren-2-yl)-4-(4-pyridylazo)aniline (BFIPy), has been designed and synthesized. BFIPy was found to have fairly good SRG-forming property in the present study.

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\text{BFIAB : } X=\text{CH} \\
\text{BFIPy : } X=N
\]

2. Experimental

BFIPy was synthesized as follows: 4-amino-pyridine (1.9 g, 20 mmol) and \(N,N'\)-bis(9,9-dimethylfluoren-2-yl)-4-nitroaniline (5.2 g, 10 mmol), which was prepared by Ullmann reaction of 4-nitroaniline and 2-iodo-9,9-dimethylfluorene.
in mesitylene in the presence of Cu, 18-crown-6, and K2CO3, were refluxed in the presence of NaOH (1.2 g, 30 mmol) in mesitylene (10 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 silicagel column chromatography using a mixed solvent of toluene and ethyl acetate as an eluent, followed by recrystallization from hexane. Yield: 1.5 g (26%), m.p.: 145 °C. MS: m/z 582 (M+). 1H NMR (750 MHz, THF-d8): δ (ppm) = 8.70 (d, 2H, J = 6.2 Hz), 7.87 (d, 2H, J = 9.0 Hz), 7.73 (d, 2H, J = 8.1 Hz), 7.71 (d, 2H, J = 7.4 Hz), 7.64 (d, 2H, J = 6.2 Hz), 7.43 (d, 2H, J = 7.4 Hz), 7.39 (s, 2H), 7.29 (dd, 2H, J = 7.4, 7.4 Hz), 7.25 (dd, 2H, J = 7.4, 7.4 Hz), 7.22 (d, 2H, J = 9.0 Hz), 7.19 (dd, 2H, J = 8.1 Hz), 1.42 (s, 12H). 13C NMR (188 MHz, THF-d8): δ (ppm) = 158.3, 156.4, 154.6, 153.1, 152.2, 147.8, 147.1, 139.6, 137.0, 127.9, 127.8, 125.9, 125.6, 123.3, 121.9, 121.8, 121.0, 120.5, 116.5, 47.7, 27.2. Calcd for C42H34N4O2: C, 84.50; H, 5.88; N, 9.61%. Found: C, 84.54; H, 5.98; N, 9.45%.

Photoinduced SRG formation was carried out by using a compact CW laser (488 nm: CYAN-488-100NH-W, Spectra Physics) as a source of writing beams. Atomic force microscopy (AFM) was performed by means of Scanning Probe Microscope (JSTM-4200D, JEOL Ltd.) with a micro cantilever (OMCL-AC160T-C2, Olympus).

3. Results and discussion

A novel photochromic amorphous molecular material, BFIPy, was synthesized by condensation of corresponding amino and nitro-substituted precursors and identified by various spectroscopy, mass spectrometry and elemental analysis.

BFIPy 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 101 °C by differential scanning calorimetry, being almost similar to that for the parent material, BFIAB (97 °C) [16].

BFIPy was found to exhibit photochromism as amorphous film as well as in solution. Fig. 1 shows electronic absorption spectral change of BFIPy amorphous film. When the film was irradiated with 450 nm-light, the absorbance around 480 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.

Using the novel photochromic amorphous molecular material, BFIPy, photoinduced SRG formation was investigated. The amorphous film was irradiated with two writing beams (488 nm) with incident angles of with +10° and −10° with respect to the normal of the sample film and with polarization angles of +45° and −45° with respect to the p-polarization at 10 mW each for 10 min at ca. 20 °C (Fig. 2). As a result, relatively large SRG was found to be inscribed, which was confirmed by AFM as shown in Fig. 3. Modulation depth of the resulting SRG was found to be 400-480 nm. The value was somewhat smaller than that of SRG inscribed on a BFIAB amorphous film under the similar conditions (ca. 500 nm) [12] even though the molecular size and Tg of BFIPy are almost similar to those of BFIAB. Difference in reactivity of photochromic reactions as amorphous films may

Fig. 1. Electronic absorption spectral change of BFIPy amorphous film. a) before photoirradiation. b) photostationary state upon irradiation with 450 nm-light.

Fig. 2. Schematic experimental setup for photoinduced SRG formation. S: sample, P: polarizer, M: mirror, W: wave plate, B: beam splitter.
affect the SRG-forming properties. Detailed photochromic properties of BFIPy as amorphous film as well as in solution are under investigation.

In summary, we have designed and synthesized a novel photochromic amorphous molecular material, BFIPy. BFIPy was found to exhibit photochromism as amorphous film as well as in solution and to have fairly good SRG-forming properties. It is expected that SRG formation of BFIPy amorphous film can be controlled by doping with appropriate hydrogen donors.

References