

## Significant Effect of Molecular Structure on Surface Relief Grating Formation for Novel Azobenzene-Based Photochromic Amorphous Molecular Materials

Hiromichi Ueda, Takahiro Tanino, Hiroyuki Ando, Hideyuki Nakano, and Yasuhiko Shiota\*  
 Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871

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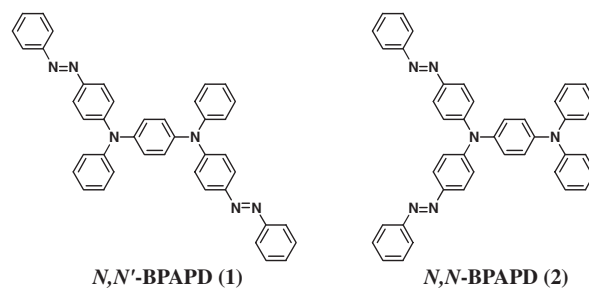
A significant effect of molecular structure on the formation of surface relief grating (SRG) was found for novel azobenzene-based photochromic amorphous molecular materials, *N,N'*-bis[4-(phenylazo)phenyl]-*N,N'*-diphenyl-*p*-phenylenediamine and *N,N'*-bis[4-(phenylazo)phenyl]-*N,N'*-diphenyl-*p*-phenylenediamine. The results provide helpful information about SRG formation.

Formation of surface relief grating (SRG) by irradiation of amorphous films of azobenzene-containing polymers with two coherent laser beams has recently received a great deal of attention in view of both academic interest and potential technological applications for erasable and rewritable holographic memory, polarization discriminator, and waveguide coupler.<sup>1–4</sup> SRG formation takes place by mass transport induced by the photoisomerization of azobenzene chromophores. Although a few models for SRG formation have been proposed,<sup>2,3</sup> detailed mechanisms have not yet been elucidated.

As a part of our studies on amorphous molecular materials,<sup>5</sup> we have proposed a new concept, "photochromic amorphous molecular materials."<sup>6–8</sup> They constitute a new class of photochromic materials that form uniform amorphous films by themselves without polymer binders. We have created a family of azobenzene-based photochromic amorphous molecular materials<sup>6,8</sup> and have shown that they also constitute a new class of promising SRG-forming materials.<sup>8</sup> We have also shown that SRG is formed more rapidly for an amorphous molecular material than for a corresponding vinyl polymer with the same pendant azobenzene chromophore.<sup>9</sup>

In order to understand the mechanism of SRG formation and to design high-performance SRG-forming materials, it is necessary to elucidate the relationship between molecular structure and SRG formation. Amorphous molecular materials, which are free from polymer chains and their entanglement, are expected to permit ready studies of the correlation between molecular structure and SRG formation. We report here a significant effect of molecular structure on SRG formation for newly designed amorphous molecular materials with two azobenzene chromophores, *N,N'*-bis[4-(phenylazo)phenyl]-*N,N'*-diphenyl-*p*-phenylenediamine (*N,N'*-BPAPD, **1**) and *N,N'*-bis[4-(phenylazo)phenyl]-*N,N'*-diphenyl-*p*-phenylenediamine (*N,N'*-BPAPD, **2**), where the positions of the two azobenzene groups in the *p*-phenylenediamine core are different from each other.

*N,N'*-BPAPD (**1**) was synthesized by the reaction of *p*-diiodobenzene (4.95 g) with 2 mol equiv. of 4-(phenylamino)azobenzene (10.4 g) in the presence of copper powder (39.0 g), K<sub>2</sub>CO<sub>3</sub> (16.6 g), and 18-crown-6 (0.81 g) in mesitylene (180 mL) at 180–185 °C for 25 h (crude yield: ca. 40%). Likewise, *N,N'*-BPAPD (**2**) was synthesized by the reaction of 4-ami-

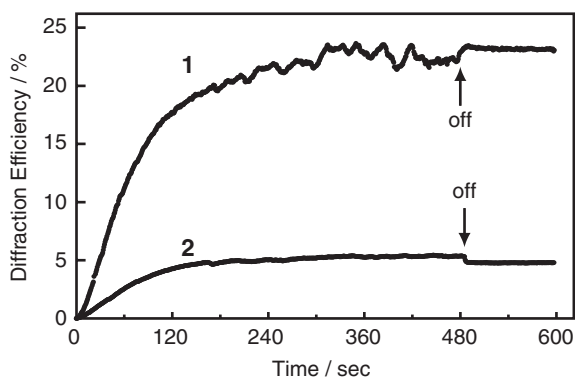


notriphenylamine (4.05 g) with 2 mol equiv. of 4-iodoazobenzene (12.1 g) in the presence of copper powder (4.63 g), K<sub>2</sub>CO<sub>3</sub> (17.5 g), and 18-crown-6 (1.00 g) in mesitylene (50 mL) at 180–185 °C for 10 h (crude yield: ca. 20%). The synthesized new compounds were purified by silica-gel column chromatography using toluene/hexane as an eluent, followed by recrystallization from toluene/acetone for **1** and THF/ethanol for **2**, and identified by various spectroscopy, mass spectrometry, and elemental analysis.<sup>10</sup>

These novel photochromic amorphous molecular materials, **1** and **2**, were found to readily form amorphous glasses with glass-transition temperatures of 80 and 78 °C, respectively, as determined by DSC. They were found to exhibit photochromism as amorphous films, undergoing *trans*–*cis* and *cis*–*trans* photoisomerizations of azobenzene chromophores; upon irradiation with 450-nm light, the absorbance of both films at their band maxima (455 nm for **1** and 450 nm for **2**) decreased to 76–78% of the original one at the photostationary state, where the rate of *trans*–*cis* photoisomerization is equal to that of the reverse *cis*–*trans* photoisomerization. The backward *cis*–*trans* isomerization also takes place thermally.

The amorphous film samples with a thickness of 40–50 μm for the experiments of SRG formation were cast from THF solution onto a glass substrate preheated at ca. 130 °C, and then allowed to cool to room temperature on standing in air. The experiments of SRG formation using the amorphous films of **1** and **2** were carried out at room temperature by the use of two linearly polarized Ar<sup>+</sup> laser beams (488 nm, 10 mW, ca. 80 mWcm<sup>-2</sup>) with polarization angles of +45° and –45° with respect to the *p*-polarization as writing beams and a He–Ne laser (633 nm) as a probe beam. The interference angle between the two writing beams was 20°. The first order diffraction efficiency, which is defined as the ratio of the intensity of the first order diffraction of the probe beam to that of the incident one, was monitored during irradiation of the sample with the two writing beams.

When the amorphous films of **1** and **2** were irradiated with the two writing beams, the diffraction efficiency gradually increased with irradiation time and almost saturated within 5 min

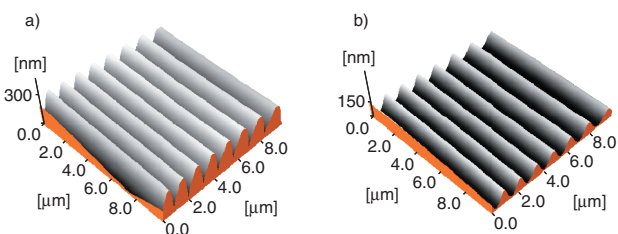


**Figure 1.** Irradiation time dependence of diffraction efficiencies for amorphous films of **1** and **2**.

(Figure 1). SRG formation was confirmed by atomic force microscopy as shown in Figure 2. A marked effect of the molecular structure on SRG formation was demonstrated. That is, while the diffraction efficiency and the modulation depth of SRG for **2** were only 5% and 120 nm, those for **1** were 20% and 240 nm. Since the glass-transition temperatures of **1** and **2** are almost the same, the ease of molecular motions is thought to be similar for **1** and **2**. Therefore, the four times greater diffraction efficiency and the doubled modulation depth for **1** relative to **2** are attributed to the difference in the molecular structure, namely, the difference in the position of the two azobenzene chromophores in the molecule.

The results are reasonably explained in terms of the anisotropic diffusion model.<sup>3</sup> Generally, the molecule containing the azobenzene chromophore effectively absorbs light with a polarization direction parallel to the long axis of the azobenzene chromophore in the molecule. The diffusion model assumes that molecules that absorbed light move to the direction parallel to the long axis of the azobenzene chromophore through the cycles of the photoinduced *trans*–*cis* and *cis*–*trans* isomerizations of the azobenzene chromophore, escaping from the site where the interference light with a stronger p-polarization component is irradiated to the site where the interference light with a weaker p-polarization component is irradiated.

In the case of the molecule **1** which contains two azobenzene chromophores parallel to each other, photoinduced mass transport along the direction parallel to the p-polarization effectively takes place to produce SRG. On the other hand, the molecule **2** where the two azobenzene chromophores are not parallel to each other can move to directions different from that parallel to the p-polarization, resulting in ineffective SRG formation. The top and its neighbor of the resulting SRG are irradiated with the interfer-



**Figure 2.** AFM Images of SRG formed on amorphous films of **1** (a) and **2** (b).

ence light with a stronger s-polarization component and weaker or non p-polarization component. At this site, the molecule **1** with the long axis of the two azobenzene chromophores parallel to the p-polarization does not effectively absorb the light, and hence they stay there. By contrast, the molecule **2** can absorb light with the s-polarization since the long axes of the two azobenzene chromophores are not parallel to each other and move so that the molecules can escape from this site, resulting in the decrease in the height of the top of the SRG.

To our knowledge, this is the first definite example that demonstrates the correlation between molecular structure and SRG formation.

In summary, the present study shows a significant effect of molecular structure on SRG formation for novel amorphous molecular materials containing two azobenzene chromophores, providing helpful information about the mechanism for SRG formation.

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- $N,N'$ -BPAPD (**1**): mp 217 °C; <sup>1</sup>H NMR (750 MHz, THF-*d*<sub>8</sub>): δ 7.12 (t, 2H, *J* = 8.5 Hz), 7.13 (d, 4H, *J* = 8.9 Hz), 7.15 (s, 4H), 7.22 (d, 4H, *J* = 7.4 Hz), 7.34 (dd, 4H, *J* = 7.4, 8.5 Hz), 7.40 (t, 2H, *J* = 7.3 Hz), 7.47 (dd, 4H, *J* = 7.3, 7.9 Hz), 7.82 (d, 4H, *J* = 8.9 Hz), 7.85 (d, 4H, *J* = 7.9 Hz); <sup>13</sup>C NMR (188 MHz, THF-*d*<sub>8</sub>): δ 122.0, 123.3, 125.1, 125.2, 126.5, 127.4, 129.8, 130.5, 131.0, 144.0, 147.8, 148.1, 151.6, 153.9; Anal. Found: C, 81.16; H, 5.28; N, 13.32%. Calcd for C<sub>42</sub>H<sub>32</sub>N<sub>6</sub>: C, 81.27; H, 5.20; N, 13.54%; λ<sub>max</sub>(toluene) (log ε): 321 nm (4.5), 440 nm (4.6).  
 $N,N'$ -BPAPD (**2**): mp 204 °C; <sup>1</sup>H NMR (750 MHz, THF-*d*<sub>8</sub>): δ 7.01 (t, 2H, *J* = 7.3 Hz), 7.08 (d, 2H, *J* = 9.0 Hz), 7.12 (d, 4H, *J* = 8.6 Hz), 7.13 (d, 2H, *J* = 9.0 Hz), 7.26 (dd, 4H, *J* = 7.3, 8.6 Hz), 7.27 (d, 4H, *J* = 8.9 Hz), 7.42 (t, 2H, *J* = 7.3 Hz), 7.49 (dd, 4H, *J* = 7.3, 7.9 Hz), 7.87 (d, 4H, *J* = 7.9 Hz), 7.88 (d, 4H, *J* = 8.9 Hz); <sup>13</sup>C NMR (188 MHz, THF-*d*<sub>8</sub>): δ 123.4, 123.9, 123.9, 125.1, 125.3, 125.4, 128.4, 129.8, 130.1, 131.3, 141.5, 146.3, 148.6, 149.0, 150.8, 153.9; Anal. Found: C, 80.99; H, 5.26; N, 13.47%. Calcd for C<sub>42</sub>H<sub>32</sub>N<sub>6</sub>: C, 81.27; H, 5.20; N, 13.54%; λ<sub>max</sub>(toluene) (log ε): 331 nm (4.5), 465 nm (4.5).