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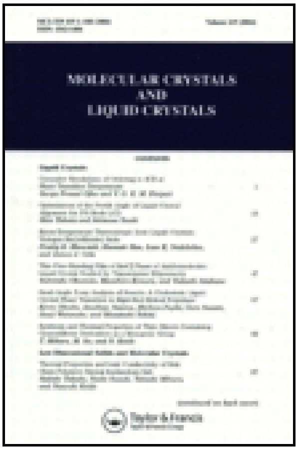

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Surface Relief Grating Formation Using a Novel Azobenzene-based Photochromic Amorphous Molecular Material, Tris[4-(phenylazo)phenyl]amine

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A novel azobenzene-based photochromic amorphous molecular material, tris[4-(phenylazo)phenyl]amine (TPAPA), was designed and synthesized. TPAPA was found to readily form an amorphous glass with a glass-transition temperature of 67°C and to exhibit photochromism as amorphous film. Irradiation of amorphous film of TPAPA with two coherent Ar^+ *laser beams led to the formation of surface relief grating with a diffraction efficiency of* 2∼3% *and a modulation depth of ca. 100 nm.*

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

INTRODUCTION

Formation of surface relief grating (SRG) by irradiation of amorphous films of azobenzene-functionalized 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, polarization discriminator, and waveguide coupler [1]. SRG formation takes place by mass transport induced by the photoisomerization of the

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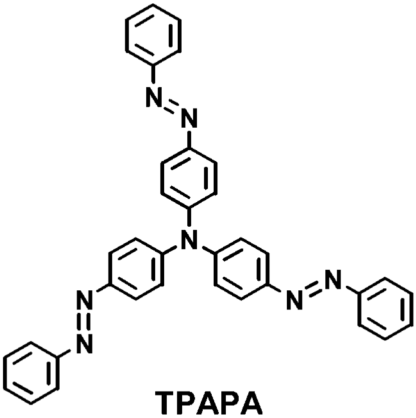
azobenzene chromophore. A few models for SRG formation have been proposed [2]; however, detailed mechanism has not yet been elucidated.

As a part of our studies on amorphous molecular materials [3], we have proposed a new concept, "photochromic amorphous molecular materials" [4] and have created two families of photochromic amorphous molecular materials based on azobenzene and dithienylethene [4–7]. Photochromic amorphous molecular materials constitute a new class of photochromic materials that form uniform amorphous films by themselves without polymer binders. They have an 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.

It is of great interest and significance to investigate SRG formation using azobenzene-based photochromic amorphous molecular materials. As compared with polymers, amorphous molecular materials provide more simple systems that are free from polymer chains and hence their entanglement for the studies of SRG formation, enabling studies of the correlation between molecular structure and SRG-forming properties. We have investigated SRG formation using azobenzene-based photochromic amorphous molecular materials and have shown that they also constitute a new class of promising SRG-forming materials [6]. Diffraction efficiencies of 7 and 23% and the modulation depths of 200 nm and 280 nm have been obtained for 4-[di(biphenyl-4-yl)amino]azobenzene ($Tg = 68°C$) and (4-[bis (9,9-dimethylfluoren-2-yl)amino]azobenzene ($Tg = 97°C$), respectively, when the polarization angles of the writing beams were $+45°$ and $-45°$ with respect to the p-polarization [6]. A significant effect of molecular structure on the formation of SRG was found for novel azobenzene-based photochromic amorphous molecular materials possessing two azobenzene chromophores, *N*,*N*′-bis[4-(phenylazo) phenyl]-*N*,*N*′-diphenyl-*p*-phenylenediamine (*N*,*N*′-BPAPD, $Tg = 80°C$) and *N*,*N*-bis[4-(phenylazo)phenyl]-*N*′,*N*′-diphenyl-*p*-phenylenediamine (*N*,*N*-BPAPD, $Tg = 78°C$) [7]. In addition, we have reported that SRG is formed more rapidly for an amorphous molecular material than for a corresponding vinyl polymer with the same azobenzene chromophore as pendant groups [8].

In the present study, we have designed and synthesized a novel azobenzene-based photochromic amorphous molecular material with three azobenzene chromophores, tris[(4-phenylazo)phenyl]amine (TPAPA), and investigated its SRG-forming properties.



TPAPA

EXPERIMENTAL

Synthesis of TPAPA

4-Aminoazobenzene (750 mg, 3.8 mmol) and 4-iodoazobenzene (2.4 g, 7.7 mmol) were refluxed in the presence of copper powder (600 mg, 9.5 mmol), K_2CO_3 (2.3 g, 17 mmol), and 18-crown-6 (200 mg, 0.76 mmol) in mesitylene (200 mL) for 6 h under nitrogen atmosphere. The resulting solution was extracted with toluene and washed with water. After the solvent was removed, the residue was chromatographed on silica-gel column using a mixed solvent of toluene and hexane as an eluent. Recrystallization from toluene/hexane gave dark red needles. Yield: 1.6 g (74%). m.p.: 206°C. MS: m/z 558 (M^+). ^{1}H NMR (THF-d_8, 750 MHz): δ (ppm) = 7.94 (d, 6H, $J = 8.7$ Hz), 7.90 (d, 6H, $J = 8.0$ Hz), 7.51 (dd, 6H, $J = 8.0$, 7.5 Hz), 7.45 (t, 3H, $J = 7.5$ Hz), 7.35 (d, 6H, $J = 8.7$ Hz). ^{13}C NMR (THF-d_8, 188 MHz) δ (ppm) = 153.8, 150.2, 149.9, 131.6, 129.9, 125.6, 125.3, 123.5. EA: Found: C, 77.47; H, 5.06; N, 17.30. Calcd for $C_{36}H_{27}N_7$: C, 77.54; H, 4.88; N, 17.58.

SRG Formation

Amorphous films with a thickness of ca. 50 μm were prepared as follows. An appropriate amount of a polycrystalline sample of TPAPA was heated to melt on a glass substrate, Kapton film was put on the melt sample, and then another glass substrate was pressed. After the sample was allowed to cool to room temperature, the Kapton film was removed.

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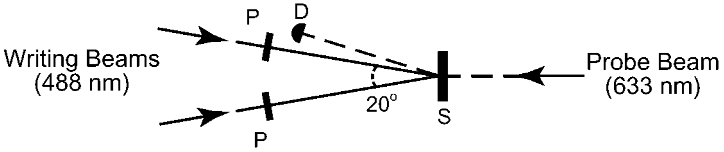

FIGURE 1 Schematic experimental setup for SRG formation. S: sample, D: detector, P: polarizer.

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SRG formation using TPAPA amorphous film was carried out by the use of an Ar^+ laser (488 nm) as two writing beams and a He-Ne laser (633 nm) as a probe beam. Experimental setup is illustrated in Figure 1.

RESULTS AND DISCUSSION

A novel azobenzene-based photochromic amorphous molecular material, TPAPA, was synthesized by the Ullmann coupling reaction of 4-aminoazobenzene with 4-iodoazobenzene.

TPAPA was found to readily form an amorphous glass when the melt sample was cooled on standing in air. The formation of the amorphous glass was confirmed by differential scanning calorimetry (DSC) and polarized light microscopy. The glass-transition temperature (Tg) of TPAPA was 67°C, as determined by DSC.

A spin-coated amorphous film of TPAPA was found to exhibit photochromism resulting from the trans-cis and the backward cis-trans isomerizations. As Figure 2 shows, the absorbance of the film at around 450 nm gradually decreased by irradiation with 450 nm-light and finally reached the photostationary state. When irradiation was stopped, the absorbance gradually recovered to the original one due to the backward thermal cis-trans isomerization.

Formation of SRG using TPAPA was investigated. The first-order diffraction efficiency, which is defined as the intensity ratio of the first order diffraction of the probe beam to the incident one, was monitored as a function of irradiation time by the measurement of the intensity of the diffracted probe beam. Figure 3a shows the irradiation time dependence of the diffraction efficiency for the amorphous film upon irradiation with the writing beams with polarization angles of $+45^\circ$ and -45° with respect to the p-polarization at a power of 10 mW (ca. 80 mW cm^{-2}). The diffraction efficiency gradually increased with irradiation time and was finally saturated. The diffraction efficiency of the SRG was found to be $2 \sim 3\%$. The formation of SRG was

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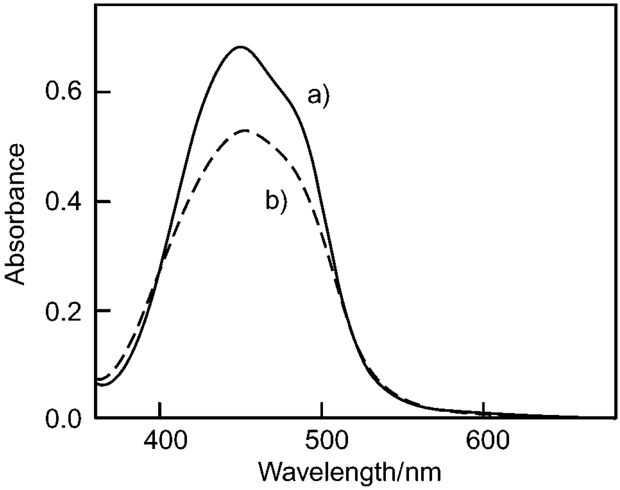
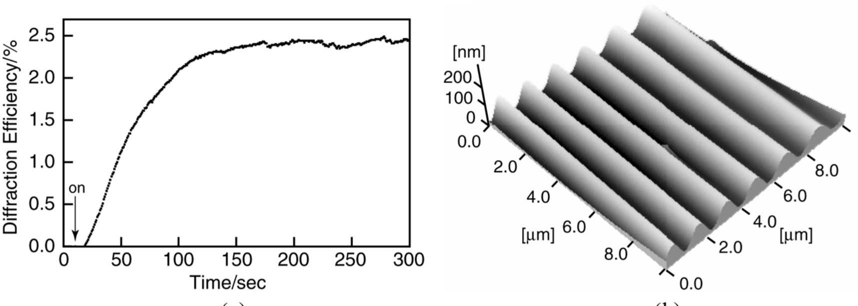


FIGURE 2 Electronic absorption spectral change of TPAPA as amorphous film. a) before photoirradiation, b) photostationary state upon irradiation with 450 nm-light.

confirmed by atomic force microscopy (AFM) as shown in Figure 2b. The modulation depth of the SRG was ca. 100 nm.

The diffraction efficiency and modulation depth of the SRG for the TPAPA amorphous film were much smaller than those for the DBAB amorphous film. The ease of molecular motions of TPAPA as amorphous film is thought to be more or less similar to that of DBAB since the Tgs of TPAPA (67°C) and DBAB (68°C) are comparable to each other. Therefore, the difference in the SRG-forming properties between



(a) (b)

FIGURE 3 a) Irradiation time dependence of diffraction efficiency for the amorphous film of TPAPA. b) AFM image of SRG formed on TPAPA film.

TPAPA and DBAB are attributed to the difference in the molecular structure. We have reported a significant effect of molecular structure on the formation of SRG for novel azobenzene-based photochromic amorphous molecular materials possessing two azobenzene chromophores, *N*,*N*′-BPAPD and *N*,*N*-BPAPD, where the positions of the two azobenzene chromophores in the *p*-phenylenediamine core are different from each other. The results have suggested that the position of the azobenzene chromophores in a molecule play an important role for SRG formation [7]. The long axes of three azobenzene chromophores in the TPAPA molecule are not parallel to one another; this may be responsible for less favorable formation of SRG relative to DBAB.

CONCLUSION

A novel azobenzene-based photochromic amorphous molecular material with three azobenzene chromophores, TPAPA, was designed and synthesized. TPAPA was found to form SRG with a diffraction efficiency of $2\sim3\%$ and a modulation depth of ca. 100 nm. Comparison of SRG formation between TPAPA and DBAB shows that the molecular structure plays an important role for SRG formation.

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