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Photoinduced Surface-relief-grating Formation Using a Mixed Film of 4-[Bis(4-methylphenyl)amino]azobenzene and 4,4′,4″-Tris[3-methylphenyl(phenyl)amino]triphenylamine

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The ability of photoinduced surface-relief-grating (SRG) formation of 4-[bis(4-methylphenyl)amino]azobenzene (BMAB) was found to be drastically enhanced by mixing with 4,4′,4″-tris[3-methylphenyl(phenyl)amino]triphenylamine (m-MTDATA) due to the increase in glass-transition temperature (T_g). The resulting SRG inscribed on the mixed amorphous film remained even after annealing at 55 °C, which was considerably higher than the T_g of BMAB. These results suggest that the m-MTDATA molecules in the mixed film were transported together with BMAB molecules upon irradiation with the writing beams.

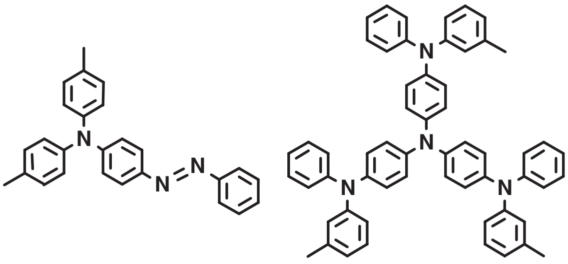
Recently, mechanical motions of materials induced by photoirradiation, refered to as photomechanical effects, have attracted a great deal of attention. Films and fibers of azobenzene-based liquid-crystalline polymers have been reported to exhibit reversible bending motions by light irradiation.[1] With regard to materials composed of low molecular-weight compounds, needle- and plate-shaped microcrystals of diarylethene, anthracene, and azobenzene derivatives have been reported to exhibit reversible bending motions and/or shape changes by photoirradiation.[2] Photoinduced surface relief grating (SRG) formation observed for films of azobenzene-based materials, which is caused by mass transport induced upon interference irradiation with coherent laser beams, is also an attractive subject of photomechanical effects.[3] Azobenzene-based materials usually exhibit excellent SRG-forming ability, although several examples of relief formation on amorphous films upon photoirradiation using materials other than azobenzene systems are known.[4] With regard to photoinduced SRG formation using azobenzene-based materials, it is believed that the mass transport is induced by trans–cis and cis–trans isomerizations of the azobenzene chromophore to produce the SRG. Several models for the mechanism of the photoinduced SRG formation have been proposed;[3b] however, the precise details are not yet clear.

We have been studying photoinduced SRG formation using azobenzene-based molecular materials, which include amorphous systems[5] and single crystals[6] of azobenzene derivatives. With regard to the amorphous systems, we have shown that increasing glass-transition temperature (T_g) of the materials is favorable for photoinduced SRG formation.[5b] As a related phenomenon, the author has also reported that azobenzene-based amorphous molecular fibers exhibit photomechanical bending motions and the bending direction of the fiber could be controllable by changing the polarization direction of the incident laser beam.[7] The result can be understood by considering the mass transport being induced at the irradiated surface of the fiber.[7]

In order to clarify the mechanism of phenomena related to the photoinduced mass transport observed for azobenzene-based amorphous systems, it is important to realize whether only molecules which undergo photochromic reactions are transported or their surrounding molecules are transported together. Hydrogen-bonded supramolecular liquid crystalline polymer systems composed of a hydrogen-bonding donor polyacrylate and an acceptor azobenzene derivative have been reported to provide photoinduced surface relief and the resulting relief structure remained even after removal of the azobenzene component.[8] Liquid crystalline thin film of azo-polymer doped with fluorescent dyes has also been reported to produce fluorescent pattern by photoirradiation through a patterned mask.[9] These facts indicate that the nonphotochromic moieties were transported together with azobenzene components. In these systems however, hydrogen bonding and/or entanglement of the polymer backbones might play an important role. Regarding mixed amorphous molecular systems without specific intermolecular interactions between azobenzene-based molecules and nonphotochromic ones, it has not been clear yet whether the nonphotochromic molecules were transported together with the photochromic azobenzene-based molecules or not upon irradiation with the writing laser beams.

The author reported here that the ability of photoinduced SRG formation of a photochromic amorphous molecular material, 4-[bis(4-methylphenyl)amino]azobenzene (BMAB), was drastically enhanced by mixing with a nonphotochromic amorphous molecular material, 4,4′,4″-tris[3-methylphenyl-(phenyl)amino]triphenylamine (m-MTDATA). The result suggested that the nonphotochromic m-MTDATA molecules were transported together with BMAB molecules. The molecular formula of BMAB and m-MTDATA are shown in Figure 1.

A sample film with a thickness of ca. 30 µm was prepared by casting an THF solution containing BMAB and m-MTDATA in a ratio of 1:4 (w/w) onto a glass substrate. The T_g of the mixed glass of BMAB and m-MTDATA with the ratio of 1:4



BMAB **m-MTDATA**

Figure 1. Molecular formula of BMAB and m-MTDATA.

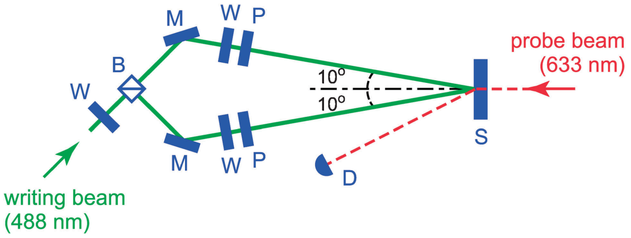


Figure 2. Schematic experimental setup for photoinduced SRG formation. S: sample, D: detector, P: polarizer, M: mirror, W: wave plate, B: beam splitter.

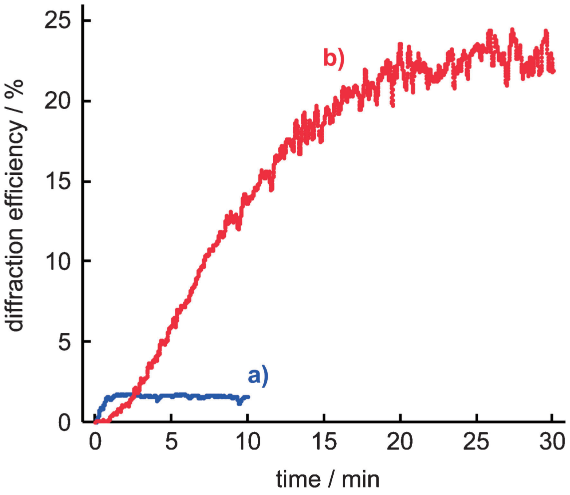


Figure 3. Growth of diffraction efficiencies for amorphous films upon interference irradiation with the writing beams. a) BMAB film. b) Mixed film of BMAB and m-MTDATA.

(w/w) was determined to be 57 °C by means of differential scanning calorimetry (DSC6220, Seiko Instruments Inc.). The schematic experimental setup for the photoinduced SRG formation was illustrated in Figure 2. Linearly polarized laser beams (488 nm: CYAN-488-100NH-W, Spectra Physics) were used as writing beams. The sample film was irradiated with the writing beams with polarization angles of +45 and −45° with respect to the p-polarization at 3 mW (ca. 95 mW cm^{-2}) each. SRG formation was monitored by diffraction efficiency of He-Ne laser beam (633 nm: HN-530P, NEOARK).

Figure 3 shows the change of diffraction efficiency upon irradiation with writing beams at 20 °C. When the BMAB film was irradiated, the diffraction efficiency increased and was saturated only ca. 1% in 1 min. Thus, the SRG-forming ability of BMAB was relatively poor as reported in our previous paper.[5b] However, the SRG-forming ability was found to be enhanced by mixing with m-MTDATA. The diffraction efficiency for the mixed film of BMAB and m-MTDATA was observed to reach ca. 23% in 30 min irradiation. The initial growing rate of diffraction efficiency for the mixed film was found to be smaller than that for the BMAB film. The result was assumed to be due to smaller content of BMAB in the mixed film. However, it is difficult to discuss in detail in the present complicated system since the diffraction efficiency was affected by not only the modulation depth of the SRG but also the refractive index.

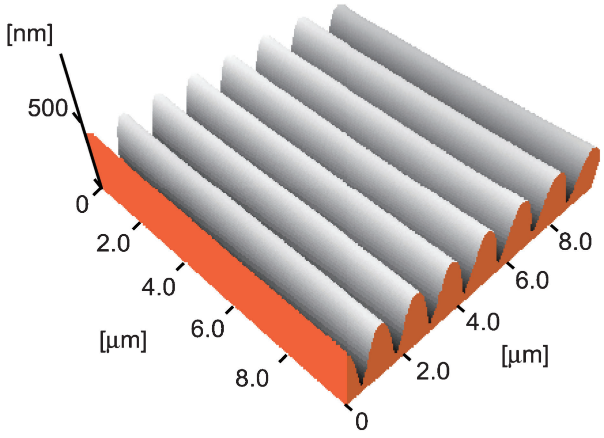


Figure 4. AFM image of SRG inscribed on the mixed film of BMAB and m-MTDATA.

SRG formation was confirmed by atomic force microscopy (AFM), performed by means of JSTM-4200D (JEOL) with a micro cantilever (OMCL-AC160T-C2, OLYMPUS). As shown in Figure 4, SRG with a modulation depth of 330–410 nm was confirmed to be inscribed on the mixed amorphous film. The modulation depth was significantly larger than that inscribed on the BMAB film (30–50 nm) under the same conditions. Thus, the mixing with m-MTDATA drastically enhanced the SRG-forming ability of BMAB.

As discussed in our previous paper,[5b] it is thought that the photoinduced SRG formation using azobenzene-based amorphous molecular materials depends upon both the photoinduced reaction as amorphous film and T_g of the material, that is the increasing frequency of trans–cis and cis–trans isomerization cycles facilitates the mass transport to grow SRG and the increasing T_g of the material prevents the collapse of the SRG due to surface tension to make the surface smooth. Since T_g of BMAB was relatively low (23 °C), the effect of the collapse of the SRG was dominant and hence just a small SRG could be inscribed. On the other hand, the SRG-forming ability was enhanced by mixing of m-MTDATA because the T_g of the mixed glass of BMAB and m-MTDATA was high enough (57 °C) to reduce the effect of the collapse of the SRG. In this consideration, the fact that the relatively large SRG could be inscribed on the mixed film at 20 °C suggests that the non-photochromic m-MTDATA molecules were also transported together with the photochromic BMAB molecules upon irradiation with the writing beams. In addition, optical microscopy (OPTIPHOTO X2, Nikon, attached with a CCD color camera VB-7010, KEYENCE) indicated that whereas the SRG inscribed on the BMAB film (Figure 5a) disappeared by annealing at 30 °C for less than 5 min (Figure 5b), the SRG inscribed on the mixed film (Figure 5c) remained even after 20 min annealing at 55 °C, which was considerably higher than the T_g of BMAB (Figure 5d). This also suggested that there existed considerable m-MTDATA molecules at the convex region of the resulting SRG. Thus, the nonphotochromic m-MTDATA molecules were suggested to be transported together with BMAB molecules upon irradiation with the writing beams. The results are expected to provide important information which helps the elucidation of the mechanism of photoinduced mass transport.

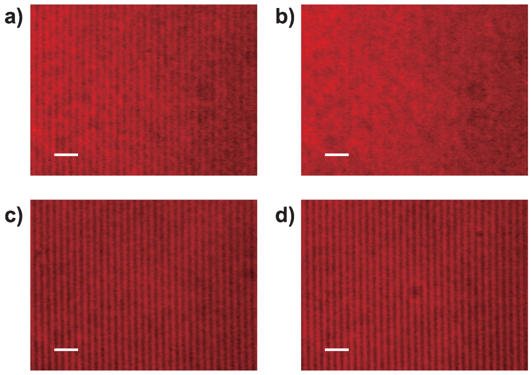


Figure 5. Photographs of optical microscope image of the films. a) SRG pattern inscribed on BMAB film. b) BMAB film after annealing at 30 °C for 5 min. c) SRG pattern inscribed on the mixed film of BMAB and m-MTDATA. d) The mixed film after annealing at 55 °C for 20 min. Scale bar: 5 µm.

It is notable that the present mixed system of BMAB and m-MTDATA provided larger SRG than the amorphous film of 4-[di(biphenyl-4-yl)amino]azobenzene (DBAB) even though the T_g of the mixed film was lower than that of DBAB (68 °C);[10] the modulation depth of the SRG inscribed on the DBAB film under the same experimental conditions as the present mixed system was 240–250 nm. It was thought that the T_g of the film decreased upon irradiation with the writing beams due to formation of cis-isomers, and hence the degree of reduction of the T_g was expected to be larger for DBAB than for the present mixed system because the much more photochromic component existed in the film of DBAB than the present mixed film. Thus, the T_g of the DBAB film upon irradiation was assumed to become lower than that of the mixed film, resulting in smaller SRG inscribed on DBAB than on the mixed film of BMAB and m-MTDATA.

In summary, it was found that a larger SRG could be inscribed on the mixed film of BMAB and m-MTDATA than the BMAB film at 20 °C and that the resulting SRG on the mixed film remained after annealing at 55 °C. These results suggest that nonphotochromic molecules existing near the photochromic molecules were transported together. Further detailed investigation is in progress.

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References

1 Y. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145; M. Kondo, Y. Yu, T. Ikeda, *Angew. Chem., Int. Ed.* **2006**, *45*, 1378; H. J. Choi, K.-U. Jeong, L.-C. Chien, M.-H. Lee, *J. Mater. Chem.* **2009**, *19*, 7124; C. L. van Oosten, C. W. M. Bastiaansen, D. J. Broer, *Nat. Mater.* **2009**, *8*, 677.
2 S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778; R. O. Al-Kaysi, A. M. Müller, C. J. Bardeen, *J. Am. Chem. Soc.* **2006**, *128*, 15938; H. Koshima, N. Ojima, H. Uchimoto, *J. Am. Chem. Soc.* **2009**, *131*, 6890.
3 a) P. Rochon, E. Batalla, A. Natansohn, *Appl. Phys. Lett.* **1995**, *66*, 136; D. Y. Kim, S. K. Tripathy, L. Li, J. Kumar, *Appl. Phys. Lett.* **1995**, *66*, 1166; P. S. Ramanujam, N. C. R. Holme, S. Hvilsted, *Appl. Phys. Lett.* **1996**, *68*, 1329; T. G. Pedersen, P. M. Johansen, N. C. R. Holme, P. S. Ramanujam, S. Hvilsted, *Phys. Rev. Lett.* **1998**, *80*, 89; A. Stracke, J. H. Wendorff, D. Goldmann, D. Janietz, B. Stiller, *Adv. Mater.* **2000**, *12*, 282; T. Ubukata, T. Seki, K. Ichimura, *Adv. Mater.* **2000**, *12*, 1675; A. Natansohn, P. Rochon, *Chem. Rev.* **2002**, *102*, 4139. b) C. Barrett, A. Natansohn, P. Rochon, *J. Phys. Chem.* **1996**, *100*, 8836; J. Kumar, L. Li, X. L. Jiang, D.-Y. Kim, T. S. Lee, S. K. Tripathy, *Appl. Phys. Lett.* **1998**, *72*, 2096; P. Lefin, C. Fiorini, J.-M. Nunzi, *Pure Appl. Opt.* **1998**, *7*, 71; N. K. Viswanathan, D. Y. Kim, S. Bian, J. Williams, W. Liu, L. Li, L. Samuelson, J. Kumar, S. K. Tripathy, *J. Mater. Chem.* **1999**, *9*, 1941; C. Fiorini, N. Prudhomme, G. de Veyrac, I. Maurin, P. Raimond, J.-M. Nunzi, *Synth. Met.* **2000**, *115*, 121; Y. B. Gaididei, P. L. Christiansen, P. S. Ramanujam, *Appl. Phys. B* **2002**, *74*, 139; K. Yang, S. Yang, J. Kumar, *Phys. Rev. B* **2006**, *73*, 165204.
4 H. Ono, A. Emoto, N. Kawatsuki, T. Hasegawa, *Appl. Phys. Lett.* **2003**, *82*, 1359; N. Kawatsuki, T. Hasegawa, H. Ono, T. Tamoto, *Adv. Mater.* **2003**, *15*, 991; T. Ubukata, K. Takahashi, Y. Yokoyama, *J. Phys. Org. Chem.* **2007**, *20*, 981; T. Ubukata, S. Yamaguchi, Y. Yokoyama, *Chem. Lett.* **2007**, *36*, 1224; T. Ubukata, S. Fujii, Y. Yokoyama, *J. Mater. Chem.* **2009**, *19*, 3373; A. Kikuchi, Y. Harada, M. Yagi, T. Ubukata, Y. Yokoyama, J. Abe, *Chem. Commun.* **2010**, *46*, 2262.
5 a) H. Nakano, T. Takahashi, T. Kadota, Y. Shirota, *Adv. Mater.* **2002**, *14*, 1157. b) H. Nakano, T. Tanino, T. Takahashi, H. Ando, Y. Shirota, *J. Mater. Chem.* **2008**, *18*, 242. c) H. Nakano, T. Takahashi, T. Tanino, Y. Shirota, *Dyes Pigm.* **2010**, *84*, 102.
6 H. Nakano, T. Tanino, Y. Shirota, *Appl. Phys. Lett.* **2005**, *87*, 061910; H. Nakano, *ChemPhysChem* **2008**, *9*, 2174; H. Nakano, *J. Phys. Chem. C* **2008**, *112*, 16042; H. Nakano, *Int. J. Mol. Sci.* **2010**, *11*, 1311; H. Nakano, S. Seki, H. Kageyama, *Phys. Chem. Chem. Phys.* **2010**, *12*, 7772.
7 H. Nakano, *J. Mater. Chem.* **2010**, *20*, 2071.
8 N. Zettsu, T. Ogasawara, N. Mizoshita, S. Nagano, T. Seki, *Adv. Mater.* **2008**, *20*, 516.
9 T. Ubukata, M. Hara, K. Ichimura, T. Seki, *Adv. Mater.* **2004**, *16*, 220.
10 T. Tanino, S. Yoshikawa, T. Ujike, D. Nagahama, K. Moriwaki, T. Takahashi, Y. Kotani, H. Nakano, Y. Shirota, *J. Mater. Chem.* **2007**, *17*, 4953.