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Thin Layers of Low Molecular Azobenzene Materials with Effective Light-Induced Mass Transport

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Azobenzene-containing film forming materials have been wellknown for the photoinduction of optical anisotropy and generation of surface relief gratings (SRG).¹ The phenomena are promising for application in optics and photonics, including diffractive optical elements, optical data storage and communications.² The formation of SRG is advantageous for many applications due to its efficiency, all-optical character and reversibility.²

The key to the photoinduced mass transport (the basic process of SRG formation) is the efficient multiple cycling between E and Z isomers of azobenzene moieties upon irradiation. Beyond this local process, the micrometer scale motion takes place that tags the passive polymer matrix and causes significant corrugation of a film surface (SRG).¹ Though the effect has been demonstrated in a plenty of azobenzene-containing materials, there is still no clear understanding of the grating formation mechanism. Most theories are based on a driving force directly applied to the azobenzene unit while differing in the nature of this force. Alternatively socalled phototriggered mechanism was proposed to explain the SRG formation in some LC azobenzene-containing materials.³ Interestingly, in the materials with phototriggered mechanism the surface corrugation as deep as double film thickness could be achieved making these materials superior to others in terms of sensitivity. However, their practical applications may be restricted by small film thickness and thus by correspondingly low values of diffraction efficiency (DE) and surface modulations reached. In this sense the supramolecular materials achieving a record modulation depth of 1650 nm^{4a} are superior to other azobenzene containing materials. Moreover, the supramolecular materials overcome the disadvantages such as complicated synthesis, difficulties with purification and low solubility of the final material.^{4,5} These materials produced via noncovalent interactions instead of covalent bonds were summarized recently.⁵

From the other hand only very recently the possibility of a simple method of synthesis of side chain epoxy-based azobenzenecontaining oligomers directly in the film has been demonstrated for the first time.^{6a} One more example is fabrication of colorless SRG, which was demonstrated in a new easy urea-bond linked material.^{6b} The success of different material approaches motivated further investigation aiming materials with good film forming properties in a wide range of thicknesses for the efficient formation of SRG. In this sense the glass forming low molecular weight materials⁷ present a promising solution. High azobenzene loading is intrinsic to them. Second, their low molecular weight is suggested to reduce chain entanglement and thus favorably influence the SRG formation. Notice that the latter suggestion has been rather adopted from the reology of polymers then confirmed by the experimental observations on SRG formation.⁸ A few results on comparison between low molecular weight and polymer materials are rather contradictory.^{9a,9d} Obviously the comparison has been complicated by different experimental conditions.

Although a number of dendritic azobenzene materials—often associated with complicated synthesis—has been published, in most of cases SRG formation has not been reported. Thus, the approach of a low molecular weight material is still promising for SRG formation. Other than already mentioned complicated synthesis the main problem to overcome is a strong tendency to crystallization or aggregation restricting film forming properties.

We report here the very effective SRG formation in the novel azobenzene-containing materials with three azobenzene units bound to the core.

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^{(1) (}a) Ichimura, K. Chem. Rev. 2000, 100, 1847. (b) Natansohn, A.; Rochon, P. Chem. Rev. 2002, 102, 4139.

^{(2) (}a) Viswanathan, N. K.; Kim, D. Y.; Bian, S.; Williams, J.; Liu, W.; Li, L.; Samuelson, L.; Kumar, J.; Tripathy, S. K. *J. Mater. Chem.* **1999**, *9*, 1941. (b) Yoshino, K.; Takeda, H.; Kasano, M.; Satoh, S.; Matsui, T.; Ozaki, R.; Fujii, A.; Ozaki, M.; Kose, A. *Macromol. Symp.* **2004**, *212*, 179. (c) Harada, K.; Itoh, M.; Yatagai, T.; Kamemaru, S. *Optic. Rev.* **2005**, *12*, 130. (d) Ye, C.; Wong, K. Y.; He, Y.; Wang, X. *Opt. Exp.* **2007**, *15*, 936.

^{(3) (}a) Úbukata, T.; Seki, T.; Ichimura, K. *Adv. Mater.* **2002**, *12*, 1675. (b) Zettsu, N.; Fukuda, T.; Matsuda, H.; Seki, T. *Appl. Phys. Lett.* **2003**, *83*, 4960. (c) Zettsu, N.; Seki, T. *Macromolecules* **2004**, *37*, 8692. (d) Zettsu, N.; Ogasawara, T.; Arakawa, R.; Nagano, S.; Ubukata, T.; Seki, T. *ibid* **2007**, *40*, 4607. (e) Zettsu, N.; Ogasawara, T.; Mizoshita, N.; Nagano, S.; Seki, T. *Adv. Mater.* **2008**, *20*, 516.

^{(4) (}a) Kulikovska, O.; Goldenberg, L. M.; Stumpe, J. Chem. Mater. 2007, 19, 3343. (b) Kulikovska, O.; Goldenberg, L. M.; Kulikovsky, L.; Stumpe, J. Chem. Mater. 2008, 20, 3528. (c) Stumpe, J.; Goldenberg, L.; Kulikovska, O. European Patent EP 1632520-A1; (d) Kulikovska, O.; Kulikovsky, L.; Goldenberg, L. M.; Stumpe, J. Proc. SPIE 2008, 6999, 69990I. (e) Kulikovsky, L.; Kulikovska, O.; Goldenberg, L. M.; Stumpe, J. ACS Appl. Mater. Interface 2009, 1, 1739. (f) Goldenberg, L. M.; Kulikovska, O.; Stumpe, J. Langmuir 2005, 21, 4794.

⁽⁵⁾ Stumpe, J.; Kulikovska, O.; Goldenberg, L. M.; Zakrevskyy, Y. In Azobenzene-Containing Polymers and Liquid Crystals; Zhao, Y., Ikeda, T., Eds.; Wiley: New York, 2009, Chapter 2, P47.

^{(6) (}a) Goldenberg, L. M.; Kulikovsky, L.; Kulikovska, O.; Stumpe, J. J. Mater. Chem. 2009, 19, 6103. (b) Goldenberg, L. M.; Kulikovsky, L.; Kulikovska, O.; Stumpe, J. J. Mater. Chem. 2009, 19, 8068; (c) Goldenberg, L. M.; Kulikovsky, L. Unpublished results.

^{(7) (}a) Shirota, Y. J. Mater. Chem. 2005, 15, 75. (b) Tanino, T.; Yoshikawa, S.; Ujike, T.; Nagahama, D.; Moriwaki, K.; Takahashi, T.; Kotani, Y.; Nakano, H.; Shirota, Y. J. Mater. Chem. 2007, 17, 4953.

⁽⁸⁾ Gharagozloo-Hubmann, K.; Kulikovska, O.; Börger, V.; Menzel, H.; Stumpe, J. *Macromol. Chem. Phys.* 2009, 210, 1809.

^{(9) (}a) Seo, E.-M.; Kim, M. J.; Shin, Y.-D.; Lee, J.-S.; Kim, D.-Y. Mol. Cryst. Liq. Cryst. 2001, 370, 143. (b) Kim, M. J.; Seo, E.-M.; Vak, D.; Kim, D.-Y. Chem. Mater. 2003, 15, 4021. (c) Chun, C.; Kim, M. J.; Vak, D.; Kim, D.-Y. J. Mater. Chem. 2003, 13, 2904. (d) Chun, C.; Seo, E.-M.; Kim, M. J.; Shin, Y.-D.; Kim, D.-Y. Opt. Mater. 2007, 29, 970. (e) Lee, E. U.; Jung, K. M.; Cho, M. J.; Kim, K. H.; Choi, D. H. Macronol. Res. 2008, 16, 434.



Figure 1. Reaction scheme.

The materials were prepared by amide formation through reaction of 1,3,5-benzenetricarbonyl trichloride (BTC) with aminosubstituted azobenzene derivative in anhydrous dimethoxyethane at room temperature in the presence of triethylamine (Figure 1) in analogy to the reaction of BTC and aniline.¹⁰ Recently, a similar compound has been patented for the use in dielectric films.¹¹ With our recipe the crude solution after filtration could be used strait away for the optical film preparation without further purification. In spite of the azobenzene loading close to 75% by weight no crystallization was visually observed in the films for at least 5 months. The thickness of the films was in the range of 50–2000 nm as measured by profilometer. The reaction could be also performed with other amino- and hydroxy-substituted azobenzene. Not all tested derivatives render film-forming properties, indicating that not in all cases the product was amorphous.

For 4-aminoazobenzene (AAB), the formation of three-armed product was proved by ESI-mass spectroscopy (m/z = 748.2836). The presence of compounds with two and one azobenzene units (m/z = 569.1967 and 392.9200) and some initial 4-aminoazobenzene (m/z = 196.9667) was also detected. By ¹H NMR spectroscopy it was estimated that ca. 10% of unreacted AAB (H₂N, ca. 4 ppm) and respectively ca. 10% of -COCl groups in BTC are left building compounds with two and/or one azobenzene arms. For comparison the product was also separated by column chromatography (silica gel, eluent CH₂Cl₂, then ethyl acetate) and recrystallized from THF:EtOH (70% yield), mp 317 °C. It was characterized by ¹H NMR [(500 MHz, DMSO- d_6 , ppm): 10.97 (s, 3H), 8.83 (s, 3H), 8.11 (d, 6H), 7.99 (d, 6H), 7.89 (d, 6H), 7.53-7.60 (m, 9H) (Figure 2)], ¹³C NMR [(75 MHz, DMSO-*d*₆, ppm): 164.7, 151.9, 148.0, 141.9, 135.2, 131.0, 129.3, 128.9, 123.5, 122.3, 120.5 (see Supporting Information)], FTIR [(KBr, cm⁻¹): 1677 and 1533 (amide)], ESI-mass spectroscopy [calculated for C₄₅H₃₄N₉O₃, 748.2785; found, 748.2804; $[M + H^+]$, 749.2781], and elemental analysis (Anal. Calcd for C45H34N9O3: C, 72.28; H, 4.48; N, 16.86. Found: C, 70.98; H, 4.58; N, 16.88). Optical films were prepared with the pure compound and compared in their holographic efficiency with the crude formulation (see below, Figure 6).

The photoinduced orientation has been investigated by exposing the films to the linearly polarized light of 488 nm with spatially homogeneous intensity of 300 mW cm⁻¹ as described before.^{4,6} The induced birefringence (Figure 3) was switched between two states by changing the polarization plane of the irradiating light. After irradiating light was switched off a slight relaxation of



Figure 2. ¹H NMR spectrum of main product of reaction between BTC and AAB.



Figure 3. Induction of birefringence Δn in a 1.97 μ m thick film of the material BTC + AAB under linearly polarized homogeneous irradiation at 488 nm, switching and relaxation of birefringence: the light was turned on at points A (polarization state A) and B (polarization state B) and turned off at the point C.

birefringence occurred with remaining value of $\Delta n = 0.042$. This result appears to correspond to the general understanding of the orientation process in the case when azobenzene is attached without flexible spacer and three chromophores might compensate each other in their movement. It is also confirmed by other examples: three-armed material with flexible spacer^{9d} exhibited a stable photoorientation while three and four-armed materials with rigidly connected azobenzenes showed only $\Delta n \sim 0.01$.^{9b,9c}

^{(10) (}a) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346. (b) Bayliff, P. M.; Feast, W. J.; Parker, D. Polym. Bull. **1992**, *29*, 265.

⁽¹¹⁾ Arayama, K.; Hiraoka, H.; Iwato, K. US Patent application, 2008 0161532.
(12) Fukuda, T.; Matsuda, H.; Shiraga, T.; Kimura, T.; Kato, M.; Viswanathan, N. K.; Kumar, J.; Tripathy, S. K. *Macromolecules* 2000, *33*, 4220.



Figure 4. (a) DE of zeroth, first, and second diffraction orders with irradiation time for a grating in a 240 nm thick film of the material based on 4-aminoazobenzene. (b) AFM image of the inscribed SRG.



Figure 5. (a) Total DE with irradiation time for gratings in the films of the material based on BTC + AAB (thickness and final SRG modulation Δh are indicated). (b) dependence of inscription rate (slope of total DE curve) on film thickness for the material based on BTC + AAB (open circles) and material described earlier^{6b,6c} (squares).

Holographic patterning-by irradiation with interference pattern at 488 nm—was performed in orthogonal ($\pm 45^{\circ}$) polarization configuration as described in our previous papers.^{4,6} This polarization configuration has been proved to be the most effective for the SRG inscription. Grating formation was monitored in situ by diffraction of a weak probe beam as it is shown in Figure 4a for a 240 nm thick film. The inscribed relief grating was then verified by AFM measurement; the surface topology is shown in Figure 4b. A relief height of 350 nm was measured that correlates with the observed DE. The achieved relief height is noteworthy as it significantly exceeds the initial film thickness. To our best knowledge it is the first demonstration of such a deep corrugation of the film surface in the relatively thin films achieved by light-induced mass transport in azobenzene-containing materials. This fact may be of high importance for the understanding of the light-induced mass transport as it is opposite to the current opinion in the literature that the mass transport can not be performed efficiently in thin films. A certain limit of thickness at the lower side is usually observed; afterward, the mass transport essentially slows down.¹² Furthermore, we investigated the dynamics of grating formation depending on film thickness in the material based on AAB. Some representative kinetics are shown in Figure 5a along with the film thicknesses and corresponding relief heights. The data are summarized in Figure 5b, where the inscription rate (slope of total DE curve) is shown with the film thickness. A clear tendency is seen-typically for the azobenzene-containing materials the gratings are formed essentially faster in thicker films until saturation is reached. However, it is noteworthy that in thinner films the surface corrugations achieved are up to 1.5 times higher than the initial film thicknesses. Even in films with thickness below 100 nm, a modulation depth of 90 nm was achieved though at higher intensity and longer irradiation time. This means that only few monolayers of the material are left in the valleys of SRG afterward. A comparison of the inscription rates for the material under study and another material^{6b}—with the typical for azobenzene-containing polymer dependency on the film thickness—is exhibited in Figure 5b. While the inscription rate for the latter polymer material becomes zero as the film thickness approaches 100 nm, the inscription rate of 0.0027 min⁻¹ was observed for the material based on BTC + AAB. We believe that high loading of azobenzene is responsible for the SRG enhancement in thin films. The understanding of this fact requires further investigations involving a theoretical consideration in terms of laminar flow.

Furthermore, we investigated the material formulations with other azobenzene derivatives. We estimated their ability to form films (glass forming properties) and the efficiency of SRG inscription. The latter was concluded from the kinetics of the total DE (Figure 6). The films with 4-amino-4'-(dimethylamino)azobenzene were even faster than the parent formulation (based on AAB). The formulation with 4,4'-diamino-derivative yielded only crystalline films. The formulation with Fast Garnet GPC (Figure 6) and pure compound based on AAB were significantly slower than the parent formulation. We also succeeded in using hydroxyl azobenzene derivative Disperse Red 13 with rather fast inscription kinetics (Figure 6); similar by structure compound was obtained recently by azo-coupling¹³ and appeared to be quite effective for holography. A surprising difference between

⁽¹³⁾ He, Y.; Gu, X.; Guo, M.; Wang, X. Opt. Mater. 2008, 31, 18.



Figure 6. Total diffraction efficiency curves for ca. 300 nm thick films of formulation with AAB, crude and pure, 4-amino-4'-(dimethylamino)azobenzene, Fast Garnet GPC, and Disperse Red 13 as indicated.

crude and pure BTC + AAB products could be explained by the material phase difference. Generally the question of the influence of the material purity on the SRG formation has been rather underevaluated in the literature. However, in the case of low molecular weight materials with high azobenzene loading it may be of high importance. Also the thermal stability of the induced structures will be influenced by the morphological state of the film.

Thermal stability of SRG in the materials under study was quite different. SRG written in the films of the material based on BTC + AAB were stable until 110-120 °C and then disappeared. SRG written in the material based on BTC + 4-amino-4'-(dimethylamino)azobenzene were very stable remaining half of their DE upon heating at high temperature (260 °C). Such high thermal stability of SRG is unusual and was found before only for ionic⁴ and urea-bond linked materials.^{6b} Correspondingly, the DSC measurements revealed a complicated phase behavior of the materials having different phase transitions during different heating cycles. Similar behavior has been reported by Shirota

et al.^{7b} For example, for the pure compound based on BTC + AAB a high temperature melting (310 °C) was observed during first heating, while the second heating revealed the glass transition at ca. 140 °C followed by polymorphism. The latter is characterized by two crystallization peaks and then by corresponding two melting peaks indicating two phases (see Supporting Information). Microscopic observation of the heated samples confirmed a melting point at ca. 317 °C. The fast cooling led to the amorphous and the slow cooling to the crystalline phase. Correspondingly to the DSC behavior the second heating under microscope observation of amorphous phase led to the crystallization at ca. 208 °C. The detailed correlation of the phase behavior with the light-induced processes may be an interesting topic for further investigation.

In summary, SRG inscription in the films based on easily prepared three arms azobenzene-containing low molecular weight glass forming materials is distinguished by high efficiency. Unusually, the induced surface corrugation can essentially exceed the initial film thickness and the inscription is still effective even in the films with thickness below 100 nm, which has not yet been reported for light-induced mass transport. This material property opens a completely new possibility to investigate the light-induced mass transport in the confinement conditions of a very thin film that was never reached before. Second, it allows application of new methods of investigations restricted to the thin films, for example surface plasmon assisted nanolithography.¹⁴ A further unique feature is a possibility to realize material transport in the true nanoscale, i.e., in films with thickness in nanometer range.

Supporting Information Available: Figures showing the DSC curves and ¹H and ¹³C NMR spectra for pure compound based on BTC and AAB. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽¹⁴⁾ König, T.; Goldenberg, L. M.; Kulikovska, O.; Kulikovsky, L.; Stumpe, J.; Santer, S. *Soft Matter*, manuscript in preparation.