

Supramolecular Azobenzene-Based Materials for Optical Generation of Microstructures

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We propose a concept of supramolecular materials for effective all-optical generation of surface relief structures and optical anisotropy. The materials are based on the ionic interactions between photochromic azobenzene units and polyelectrolytes. The materials are easy to produce and they allow the inscription of the 1.8 μm deep surface relief gratings. Moreover, the induced structures were thermally very stable. Both distinctive features of the new materials, namely, the dynamic behavior of molecular orientation and the high thermal stability of surface structures, have been explained in terms of the network of oppositely charged ions inherent to the materials. Due to the simplicity and versatility of the concept, the new family of materials for different applications in optics, sensorics, and biology may be designed.

1. Introduction

Azobenzene-containing materials have been well-known for the induction of optical anisotropy upon irradiation with polarized light.^{1,2} Recently, the formation of surface relief gratings (SRGs) in films of azobenzene-functionalized polymers under holographic exposure has been demonstrated.^{3,4} Anisotropic films, birefringence gratings, and SRG have a large potential for applications in optics and information technologies.^{5–7} In this respect the material availability, low cost, and environmentally friendly processing become of high importance. Azobenzene-functionalized polymers have been mostly used for SRG formation; however, they are quite expensive because of multistep synthesis.

Photoinduction of both optical anisotropy and SRG have been ascribed to the azobenzene chromophores capable of E-Z photoisomerization. While the optical anisotropy is due to the polarization selective absorption and reorientation of the azobenzene units, the formation of SRG implies their translational motion on the scale of micrometers. The light-induced motion of the photochromic units eventually involves covalently attached polymer backbones resulting in microscopic mass transport. It has been agreed in the literature that the presence of the azobenzene moieties covalently

bound to the polymer chains is essential for SRG formation.^{8–11} The glassy state of the materials provides for stability of molecular orientation and SRG. Precisely the azobenzene-functionalized polymers have been mostly used to generate anisotropy and surface relief gratings.^{9,12} A big drawback of those systems is the multistep synthesis required for each combination of polymer and chromophore, which makes them rather expensive for applications. Recently, we demonstrated^{13,14} an effective induction of the optical anisotropy and SRG in the azobenzene-containing polyelectrolyte PAZO (Sigma-Aldrich). Alternative use of low molecular weight glass-forming materials^{15–19} is restricted by special design and synthesis as well. “Guest–host” systems consisting of polymer matrix doped with azobenzene dyes present a cost-effective solution. However, dye aggregation limits the doping level and the SRG formation is ineffective.^{8,20}

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- (1) Todorov, T.; Tomova, N.; Nikolova, L. *Opt. Commun.* **1983**, *47*, 123.
- (2) Ivanov, M.; Todorov, T.; Nikolova, L.; Tomova, N.; Dragostinova, V. *Appl. Phys. Lett.* **1995**, *66*, 2174.
- (3) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166.
- (4) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136.
- (5) Fukuda, T.; Kim, J. Y.; Barada, D.; Yase, K. *Proc. SPIE* **2006**, *6136*, 61360.
- (6) Lu, X.; Lee, F. K.; Sheng, P.; Kwok, H. S.; Chigrinov, V.; Tsui, O. K. C. *Appl. Phys. Lett.* **2006**, *88*, 243508.
- (7) Baac, H.; Lee, J.-H.; Seo, J.-M.; Park, T. H.; Chung, H.; Lee, S.-D.; Kim, S. J. *Mater. Sci. Eng. C* **2004**, *24*, 209.

- (8) Fiorini, C.; Prudhomme, N.; de Veyrac, G.; Maurin, I.; Raimond, P.; Nunzi, J.-M. *Synth. Met.* **2000**, *115*, 121.
- (9) 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.
- (10) Zucolotto, V.; He, J.-A.; Constantino, C. J. L.; Barbosa Neto, N. M.; Rodrigues, J. J., Jr.; Mendonca, C. R.; Zilio, S. C.; Li, L.; Aroca, R. F.; Oliveira, O. N.; Kumar, J. *Polymer* **2003**, *44*, 6129.
- (11) Oliveira, J.; Osvaldo N.; dos Santos, J.; David S.; Balogh, D. T.; Zucolotto, V.; Mendonca, C. R. *Adv. Colloid Interface Sci.* **2005**, *116*, 179.
- (12) Natansohn, A.; Rochon, P. *Chem. Rev.* **2002**, *102*, 4139.
- (13) Goldenberg, L. M.; Kulikovska, O.; Stumpe, J. *Langmuir* **2005**, *21*, 4794.
- (14) Stumpe, J.; Goldenberg, L.; Kulikovska, O. PCT Patent application WO 2006/061419 A2.
- (15) Yip, W. C.; Kwok, H. S.; Kozenkov, V. M.; Chigrinov, V. G. *Displays* **2001**, *22*, 27.
- (16) Nakano, H.; Takahashi, T.; Kadota, T.; Shirota, Y. *Adv. Mater.* **2002**, *14*, 1157.
- (17) Ando, H.; Takahashi, T.; Nakano, H.; Shirota, Y. *Chem. Lett.* **2003**, *32*, 710.
- (18) Perschke, A.; Fuhrmann, T. *Adv. Mater.* **2002**, *14*, 841.
- (19) Ishow, E.; Lebon, B.; He, Y.; Wang, X.; Bouteiller, L.; Galmiche, L.; Nakatani, K. *Chem. Mater.* **2006**, *18*, 1261.
- (20) Si, J.; Qiu, J.; Zhai, J.; Shen, Y.; Hirao, K. *Appl. Phys. Lett.* **2002**, *80*, 359.

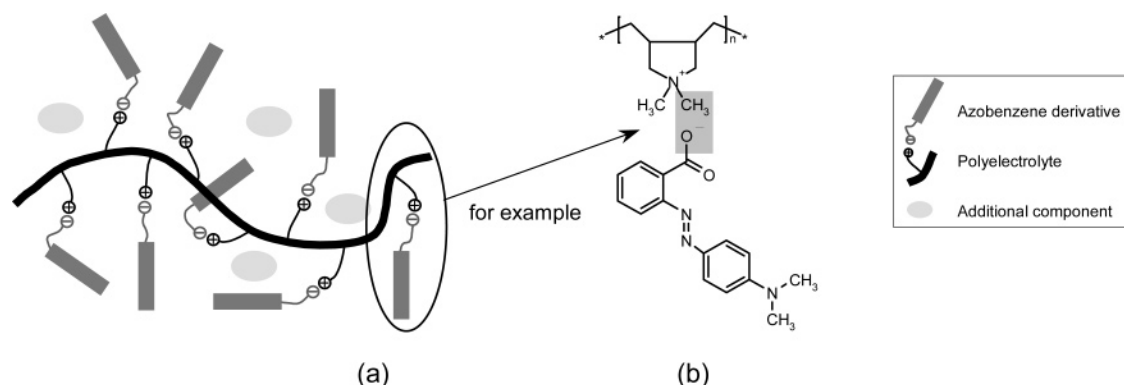


Figure 1. Schematic presentation of an azobenzene-based supramolecular material with ionic interactions (a); an example of complex formation (b).

Another approach has been based on the electrostatic layer-by-layer (LbL) deposition technique.^{10,20–26} The films consisting of adjacent layers of oppositely charged polyelectrolyte and azobenzene-containing polyelectrolyte^{20–23} or ionic azobenzenes possessing at least two ionic groups^{10,24,25} have been used for the induction of optical anisotropy and SRG. According to Zucolotto et al.,¹⁰ the electrostatic interaction between active and inert layers serves as a mean for the SRG formation but, on the other hand, tends to hinder the photoisomerization. This inherent conflict explains the poor efficiency of SRG inscription. The gratings with amplitudes of no more than 140 nm have been reported.²² A further disadvantage of this approach is the tedious and time-consuming film preparation. Thus, it is still a challenge to find commercially available low-cost systems capable of the light-induced formation of SRGs.

We propose here a new class of azobenzene-containing materials based on ionic interactions (Figure 1) and demonstrate the effective formation of SRGs. A variety of materials with targeted properties may be easily formulated from readily available and inexpensive commercial components.

2. Experimental Section

Materials. Chemical structures of the compounds described in this paper are shown in Figure 2.

Complex C–F. Fifty-four milligrams (0.082 mmol) of 5-(3-nitrophenylazo)salicylic acid, sodium salt (compound C, dye content 50%, Aldrich) in 20 mL of distilled water was mixed with 12 mg (0.082 mmol) of 30% aqueous solution poly(ethylene imine) (PEI, compound F, Polyscience). The deposit was separated by filtration, washed by MeOH, and dissolved in 1 mL of THF.

Complex B–F. Sixty-three milligrams (0.07 mmol) of (bis-4,4'-(4-hydroxy-phenylazo)styrene)-2,2'-disulfonic acid, disodium salt (compound B, dye content 70%, Aldrich) was dissolved in 5 mL of MeOH, filtrated, and mixed with 13 mg (0.08 mmol) of 30% poly(ethylene imine). Some deposit was separated and the red mother solution was used for film preparation.

Complex A–E. Thirty-seven milligrams (0.13 mmol) of 2-(4-dimethylaminophenylazo)benzoic acid, Na salt (compound A, Aldrich) in 1 mL of MeOH was mixed with 110 mg (0.13 mmol) of 20% aqueous solution of poly(diallyldimethylammonium chloride) (PDADMAC, compound E, Aldrich, molecular weight 400–500 × 10³). After filtration the solution was directly used for the film preparation.

The films of about 2 μm thickness were prepared from the above-described solutions by casting at room temperature in a closed chamber.

Measurements. FTIR spectra were measured by a Mattson Instruments RS 10000 FTIR spectrometer using the film cast onto CaF₂ substrates.

For induction of optical anisotropy the films were irradiated homogeneously with an extended beam of an Ar⁺ ion laser at the wavelength of 488 nm. The beam was polarized linearly with a polarization plane at 45° or, alternatively, at –45° and its intensity was equal to 230 mW/cm². The optical anisotropy was probed by the weak beam of a He–Ne laser at 633 nm polarized linearly horizontally. By means of a Wollaston prism, the transmitted beam was divided into two beams polarized parallel and orthogonal to the polarization plane of the incident beam. The intensities of both parallel and orthogonal polarization components were measured.

For SRG inscription the films were irradiated with the interference pattern of two orthogonally polarized beams from an Ar⁺ ion laser operating at the wavelength of 488 nm. The beams were polarized linearly with polarization planes at ±45° to the incidence plane. The angle between two interfering beams was about 12°, resulting in a period of 2.3 μm. The intensities of irradiating beams were equal to 250 mW/cm². The grating formation was probed by diffraction of a weak probe beam from a He–Ne laser. The intensities of 0th, ±1st, and ±2nd diffraction orders were measured during grating recording. The surface relief gratings were then verified by atomic force microscopy performed at Solver P47H Smena (NTMDT, Russia) in semicontact mode.

3. Results and Discussion

The basic idea of this investigation was to use intermolecular forces to keep photochromic units attached to the polymer backbones. We have proposed a new approach—photochromic supramolecular materials—and created a novel family of such film-forming materials capable of effective generation of optical anisotropy and SRGs.^{14,27} So far, noncovalent intermolecular interactions between the dye and

- (21) Park, M.-K.; Advincula, R. C. *Langmuir* **2002**, *18*, 4532.
- (22) Zucolotto, V.; Mendonca, C. R.; dos Santos, D. S.; Balogh, D. T.; Zilio, S. C.; Oliveira, O. N.; Constantino, C. J. L.; Aroca, R. F. *Polymer* **2002**, *43*, 4645.
- (23) Wang, H.; He, Y.; Tuo, X.; Wang, X. *Macromolecules* **2004**, *37*, 135.
- (24) Kaneko, F.; Kato, T.; Baba, A.; Shinbo, K.; Kato, K.; Advincula, R. C. *Colloids Surf. A* **2002**, *198–200*, 805.
- (25) He, J.-A.; Bian, S.; Li, L.; Kumar, J.; Tripathy, S. K.; Samuelson, L. *J. Phys. Chem.* **2000**, *104*, 10513.
- (26) Ziegler, A.; Stumpe, J.; Toutianoush, A.; Tieke, B. *Colloids Surf. A* **2002**, *198*, 777.

- (27) Stumpe, J.; Goldenberg, L.; Kulikovska, O. PCT Patent application, WO 2006/02450 A1.

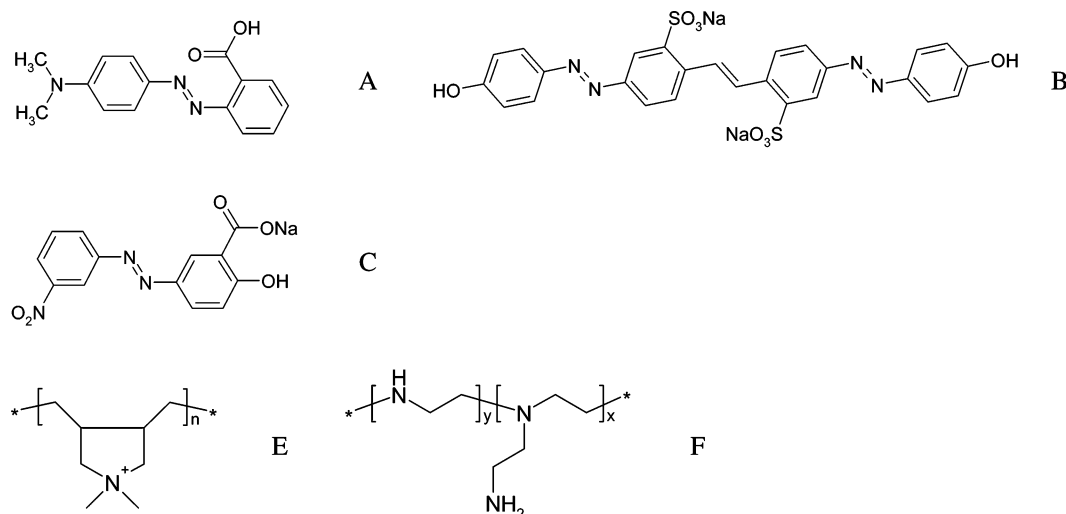


Figure 2. Examples of compounds used for materials preparation: A–C, azobenzene derivatives; E–F, polyelectrolytes.

the polymer matrix have received less attention.^{16,27,28} More attention has been recently paid to polyelectrolyte–surfactant and polyelectrolyte–polyelectrolyte complexes.^{29–34} For example, Voit and co-workers^{29,30} demonstrated supramolecular complex formation with diazosulfonate-containing polyelectrolytes. All aspects of polyelectrolyte–surfactant complexes have been reviewed recently.³⁴

In this study ionic azobenzene moieties attached to the oppositely charged polyelectrolytes by ionic interactions form complexes, as it is schematically shown in Figure 1. As active components, we used commercially available charged azobenzene derivatives (Figure 2, A–C). A highly branched polyelectrolyte, PEI, with high charge density and a polyelectrolyte with quite stiff backbone, PDADMAC, were used as polymer counterparts (Figure 2, E–F). Different functional groups and charge densities provide for the different strengths of ionic interactions. Both the interaction strength and the molecular conformation are expected to influence the light-driven mass transport. The materials were produced by mixing of water–alcohol solutions of the azobenzene derivatives and the polyelectrolytes. The formation of complexes has been proved by FTIR spectroscopy. The strong C=O stretching band of the carbonic acid³⁵ present in the original spectrum of the neutral azobenzene derivative (e.g., 2-(4-dimethylaminophenylazo)benzoic acid, Figure 2A) at 1700 cm^{-1} disappears from the spectrum of the complex in the film, indicating the formation of carboxylate anion (Figure 3). This new material concept offers wide possibilities for material design free of any complicated synthesis and tedious film-making procedures. At the same time it provides for a mechanism for active units to drag the inert component when

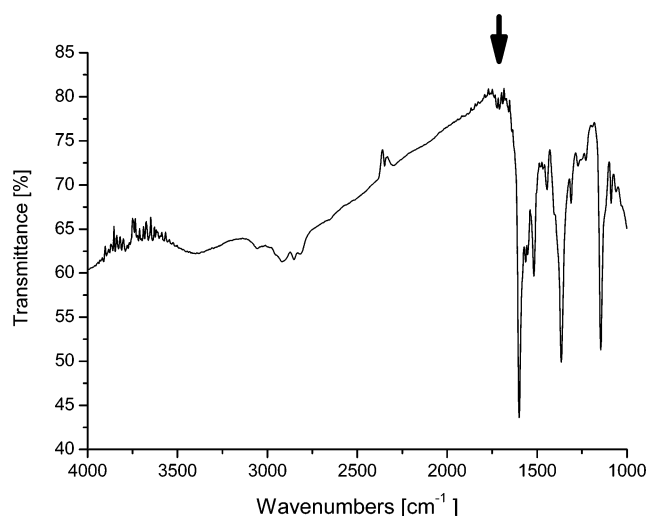


Figure 3. FTIR spectra of films obtained from complex of azobenzene derivative A with F; the arrow indicates the position of possible C=O stretching vibration.

moved by the light. In this way the proposed concept combines the efficiency of functionalized polymers with simplicity and cost effectiveness of “guest–host” systems, avoiding complexity and disadvantages of LbL films.

The materials were readily processed into films by conventional film-building techniques (spin coating, casting, etc.). If the complex was precipitated, the product was separated and dissolved in another solvent. Otherwise, the complexes were sufficiently soluble in a water–alcohol mixture to form films of good optical quality and desired thickness directly from these solutions.

The irradiation of the films with linearly polarized light led to the induction of optical anisotropy that is due to the orientation of chromophores. In the materials under investigation it was found unstable in contrast to the most functionalized glassy polymers. Figure 4a displays the induction and relaxation of optical anisotropy in a film of the material C–F. Homogeneous irradiation of the film at 488 nm gives rise to the orthogonal polarization component of the transmitted probe beam (633 nm) absent in the incident beam, indicating the induction of optical anisotropy. After

- (28) Priimagi, A.; Cattaneo, S.; Ras, R. H. A.; Valkama, S.; Ikkala, O.; Kauranen, M. *Chem. Mater.* **2005**, *17*, 5798.
- (29) Thünemann, A. F.; Schnöller, U.; Nuyken, O.; Voit, B. *Macromolecules* **1999**, *32*, 7414.
- (30) Thünemann, A. F.; Schnöller, U.; Nuyken, O.; Voit, B. *Macromolecules* **2000**, *33*, 5665.
- (31) Thünemann, A. F.; Beyermann, J. *Macromolecules* **2000**, *33*, 6878.
- (32) Thünemann, A. F.; Lochhaas, K. H. *Langmuir* **1999**, *15*, 4867.
- (33) Thünemann, A. F.; Rupelt, D. *Langmuir* **2001**, *17*, 5098.
- (34) Thünemann, A. F. *Prog. Polym. Sci.* **2002**, *27*, 1473.
- (35) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1981.

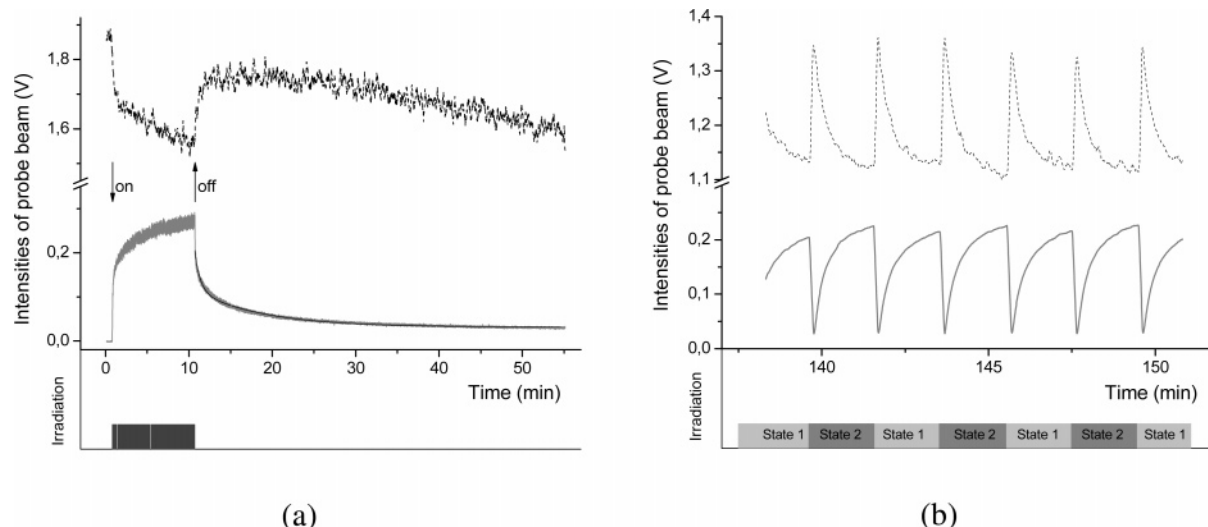


Figure 4. Optical anisotropy induced by the light in a film of the compound C-F: kinetics of the parallel (dashed black line) and orthogonal (solid gray line) polarization components of the transmitted probe beam. (a) Induction and relaxation, solid black line presents two-exponential decay fit to the data; (b) switching by alternation of polarization of the irradiating beam.

switch-off of the actinic light, the induced anisotropy relaxes, whereas the relaxation is well described by a two-exponential decay function. Alternation of the polarization of the actinic light allows switching of the induced molecular orientation as it is demonstrated in Figure 4b. We believe the observed instability of the light-induced orientation of chromophores is caused by the ionic nature of the azobenzene-polyelectrolyte materials. Unlike in the functionalized polymers,^{36,37} here polymer chains provide additionally for a spacial distribution of charges that counteracts the orientation effect of polarized light, returning the ionic chromophores to their initial positions.

For the SRG recording we used holographic and mask irradiation at 488 nm. The most effective surface structures were recorded holographically by interference of two orthogonally polarized beams. The recording times were varied from a few minutes up to 2 h at rather moderate beam intensities. An example of the recording kinetics is shown in Figure 5. Under the above experimental conditions the first-order diffraction efficiency of 40% was reached in 10 min of recording in a film of the material A-E. And already after 20 min 99% of the probe light was diffracted by the recorded grating. One can see that the diffraction behavior is typical for very deep gratings. Indeed, a grating height of ca. $1.65\ \mu\text{m}$ was confirmed by AFM measurements. The period of the grating was measured to be $2.3\ \mu\text{m}$ in accordance with the period of the interference pattern (Figure 6a). A very high efficiency of the grating formation was demonstrated also for the material A-F, where the $1.8\ \mu\text{m}$ deep surface relief grating was inscribed under similar recording conditions. In comparison, the compositions based on the azobenzene derivatives B and C were less effective, though up to 600 nm deep gratings were inscribed in these materials as well.

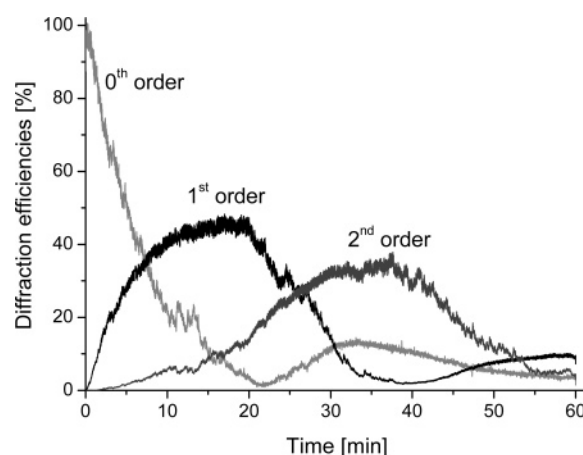


Figure 5. Diffraction efficiencies of the 0th, 1st, 2nd diffracted orders as functions of recording time. The SRG was recorded in a film of the complex A-E.

The inscribed gratings could be overwritten by subsequent recording. For example, a square structure was generated by successive inscription of two linear gratings with orthogonal grating vectors. An AFM image of such structure recorded in the complex A-E is presented in Figure 6b.

The inscribed gratings could be erased, when homogeneously irradiated with properly polarized light. For example, the grating inscribed in complexes A-F and C-F were erased by irradiation with linearly polarized light at 488 nm during 1 h. Erasing with UV light was more effective. For the material A-F the 0th diffraction order efficiency increased from 7% to 90% during 1 min irradiation with UV lamp, indicating the erasure of grating. Afterward, SRGs could be written again onto the same film.

Remarkably, at the same time the inscribed SRGs are thermally very stable. For example, the gratings inscribed in the material based on the compound C-F were erased only by heating above $150\ ^\circ\text{C}$. Notice for comparison that SRGs inscribed in azobenzene-functionalized polymers are stable only when kept below the glass transition temperature of the polymers. For example, thermally stable SRGs

(36) Fukuda, T.; Kim, J. Y.; Barada, D.; Senzaki, T.; Yase, K. *J. Photochem. Photobiol. A* **2006**, *183*, 273.

(37) Kulikovska, O.; Gharagozloo-Hubmann, K.; Stumpe, J. *Proc. SPIE* **2002**, *4802*, 85.

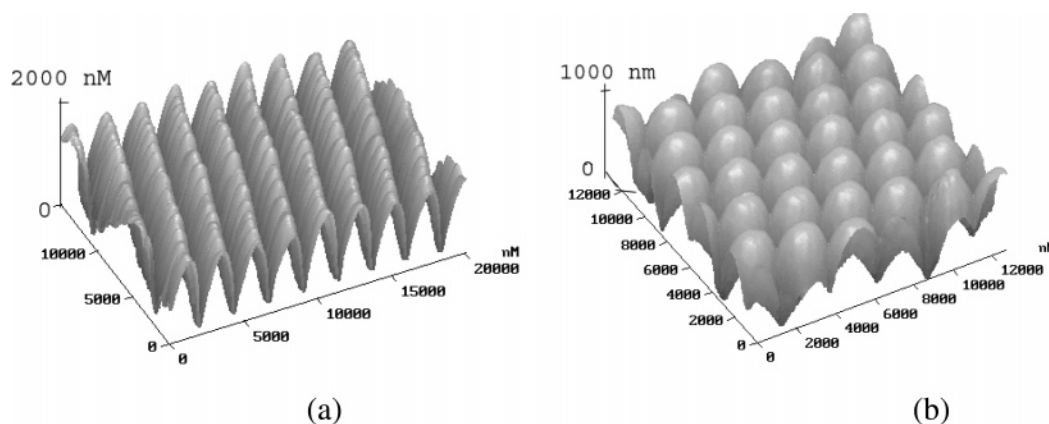


Figure 6. AFM images of SRGs recorded in the material based on the complex A–E: (a) linear grating; (b) grating resulting from successive recordings of two linear gratings with orthogonal grating vectors.

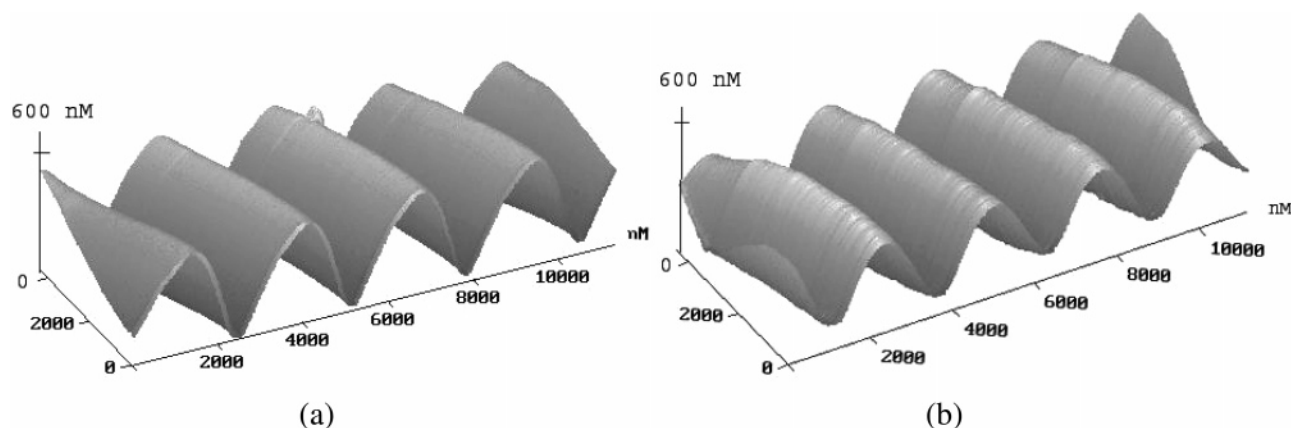


Figure 7. AFM images of SRG written in the film of material A–E (a) and PDMS replica of the same SRG (b).

reported in the literature were based on urethane–urea copolymer and were stable even at T_g of the copolymer (150 °C).³⁸ However, the inscription of the gratings was not effective with diffraction efficiencies below 1.5%.^{38,39} In general, the higher T_g of the polymers, the lower the efficiency of the SRG formation process.^{38,39} The observed combination of extraordinary thermal stability of the inscribed surface structures with the high efficiency and particularly with light reversibility is rather unique to the proposed class of materials.^{13,14,27} We believe that whereas the high efficiency is provided by the strong interaction of the chromophores with polyelectrolyte chains, the extremely high thermal stability of SRG is related to the ionic nature of these interactions, in contrast to the literature opinion that the glassy state inherent to the functionalized polymers and molecular glasses solely provides for the SRG stability. In this latter case the SRGs are induced in the glassy state that stabilizes both the orientational order and the topological structures. In contrast to that, in the new azobenzene–polyelectrolyte materials the mass transport occurs in a network of oppositely charged ions. This network is the crucial factor for both the dynamical character of the orientational order and the high thermal stability of the

induced surface structures. This suggestion may be confirmed by previously reported thermal stability of gratings in PAZO.^{13,14} Moreover, the ionic interactions seem to benefit also the film-forming properties of the materials.

Replication of induced SRGs in other materials is very important for many applications. SRGs inscribed in the materials under investigations were easily replicated by PDMS (Figure 7), Norland UV-adhesive (NOA), and PMMA. PDMS copies, for example, can be used for different soft lithographic techniques.⁴⁰

4. Conclusions

In summary, we have proposed a new type of supramolecular materials for optical manipulation and demonstrated the effective all-optical generation of surface relief structures. The materials are based on the ionic interactions between ionic azobenzene derivatives and polyelectrolytes. They are easy to make from readily available and inexpensive commercial components by processing from environmentally friendly water–alcohol solutions using conventional film-forming techniques. This new class of materials is characterized by the unique combination of high efficiency of surface relief gratings formation and of their thermal stability. In contrast to the polymers, the light-induced orientation of

(38) Che, Y.; Sugihara, O.; Fujimura, H.; Okamoto, N.; Egami, C.; Kawata, Y.; Tsuchimori, M.; Watanabe, O. *Opt. Mater.* **2002**, *21*, 79.

(39) Lee, T. S.; Kim, D. Y.; Jiang, X. L.; Li, L.; Kumar, J.; Tripathy, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 283.

(40) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550.

chromophores was found to be dynamic and was used for switching optical anisotropy. The combination of high light-induced molecular mobility and thermal stability of the induced relief structures has been ascribed to the ionic nature of the intermolecular interactions, namely, to the existing network of oppositely charged ions.

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