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From partial to complete optical erasure of azobenzene–polymer gratings: effect of molecular weight†

Jaana Vapaavuori,*[ab] Robin H. A. Ras,[a] Matti Kaivola,[a] C. Geraldine Bazuin[b] and Arri Priimagi*[ac]

The ability to control surface functionality by optical inscription and erasure of surface patterns is highly appealing, since it opens up the possibility for the design of complex, spatially varying surface topographies. We show through a supramolecular approach, which allows us to attach nominally equal amounts of azobenzene into polymers of varying molecular weight, that the completeness of optical erasure of high-modulation-depth surface-relief gratings on polymer–azobenzene complexes depends on the molecular weight of the polymer, and therefore on the glass transition temperature of the material used. The optical erasure is further applied to realize surface patterns with varying grating vector directions through masking. All patterning is done at a temperature well below the glass transition temperatures of the materials, which allows different patterning steps to be frozen into the material.

Introduction

Light provides a precise and non-invasive method to control the properties of azobenzene-containing materials. Illumination of these materials can induce actuation over large length scales, beginning with the molecular-scale photoisomerization process[1,2] and emerging into visually observable macroscopic motions.[3–7] Arguably, the widest application prospects of photoinduced motions in azobenzene-based materials lie in all-optical inscription of surface-relief gratings (SRGs), triggered by macroscopic photoisomerization-induced mass transport under light interference patterns.[4,6,8] These optically tunable patterns can reach a modulation depth of hundreds of nanometers as compared to the flat surface before illumination[9–11] and there is a growing interest in applying azobenzene-based diffraction gratings in photonics and micro-/nanofabrication.[8,12] Many of the proposed applications would benefit from light-powered erasing and rewriting of SRGs, so that the function provided by the surface pattern could be turned "on" and "off" at will.

It is well-established that SRGs in amorphous materials can be erased by heating the film above the glass transition temperature (T_g) of the material, and, if no photodegradation occurs, the patterns can be rewritten.[6,13] However, optical erasure at ambient temperature would be more appealing in terms of precise spatial control that, on top of other virtues, can be applied remotely, as opposed to global heating of the thin films. The current knowledge on the optical erasure processes of these surface topographies remains non-unified, partly because it seems to depend highly on the material's properties. Luca and co-workers have demonstrated, using low-T_g azo-polysiloxanes, that when the T_g of the studied system is too low, the optically inscribed surface patterns tend to self-erase, although this self-erasure can be accelerated by irradiation with a Gaussian beam.[14] In liquid-crystalline (LC) polymers, in which the SRG formation mechanism is related to light-induced isotropization of the LC phase,[15] Zettsu and Seki demonstrated complete and rapid erasure of SRGs inscribed in a soft liquid-crystalline polymer ($T_g = 8$ °C) by irradiation with non-coherent, non-polarized 365 nm light.[16] In the same spirit, Broer and coworkers have shown that dynamic protrusions upon illumination can be created in LC polymers due to a photoinduced change in the order parameter in the chiral nematic phase.[17,18] These jagged surface patterns self-erased within 10 s after turning off the illumination.

In amorphous materials having a T_g above ambient temperature, for which inscribed SRGs are stable for long times, even years,[6] complete ambient-temperature optical erasure of high-modulation depth SRGs remains challenging, with only partial erasure[19–22] and unsuccessful erasure attempts[23] reported. Kumar and co-workers were the first to investigate the optical erasure of photoinduced SRGs, concluding that erasure was most efficient when the erasing

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[a] *Department of Applied Physics, Aalto University, P.O. BOX 13500, FI-00076 Aalto, Espoo, Finland*

[b] *Département de chimie, Université de Montréal, C.P. 6128, Succursale Centre-Ville, Montréal (QC), Canada H3C 3J7. E-mail: jaana.vapaavuori@umontreal.ca*

[c] *Department of Chemistry and Bioengineering, Tampere University of Technology, P.O. Box 541, FI-33101 Tampere, Finland. E-mail: arri.priimagi@tut.fi*

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beam was polarized along the grating vector direction.[20] However, a remnant grating of more than 10 nm remained. Later, Lagugné-Labarthet and co-workers showed that 35 nm depth SRGs can be optically erased to less than 10 nm (although the diffraction signal did not return to zero) by applying a uniform laser beam onto the sample surface.[21] For gratings deeper than 100 nm, their erasure attempts left significant remnant gratings.[21] In 2005, Ubukata and co-workers devised optically reconfigurable distributed-feedback lasers, achieving 91% optical erasure of 35 nm azopolymer SRGs, leaving a remnant grating of 3 nm (with no attempts to erase deeper gratings reported).[22] Subsequently, the lasing wavelength could be reconfigured through inscription of an SRG with a different period. Recently, Ambrosio *et al.* showed partial erasure of surface-relief patterns with non-polarized UV illumination.[19] Conversely, enhancement in modulation depth upon uniform illumination has been reported.[24,25] These investigations raise the questions as to what material parameters make some SRGs (almost) completely erasable, whereas others remain partially or fully photostable, and also if it is possible to completely erase high-modulation-depth gratings.

Here, we address these questions using supramolecular polymer–azobenzene complexes. These complexes provide a powerful toolbox for efficient SRG-forming materials,[26–30] as they allow for easy optimization over, *e.g.*, the concentration of the active azobenzene guest molecules and the type and size of the passive host material. We take advantage of the ability to attach an equal amount of azobenzene molecules by hydrogen bonding to short polymers (oligomers) of selected molecular weights. We show that the molecular weight, with its effect on the T_g, is critical not only for the efficiency of the grating formation but also for the effectiveness of optical erasure. Moreover, even high-modulation-depth SRGs can be completely erased optically as long as the molecular weight, and hence the T_g, of the polymer host is in an appropriate range. Erasing and rewriting patterns at a working temperature that is more than 30 °C below the T_g of the material allows the patterning to be frozen in, facilitating the preparation of complex surface architectures. As a model demonstration, we construct a multi-patterned SRG with patterns of varying grating vector directions.

Experimental

The supramolecular complexes studied, shown in Fig. 1a, consist of 4-hydroxy-4′-dimethylaminoazobenzene (241 g mol^{-1}; TCI Europe) and poly(4-vinyl pyridine) (P4VP; Polymer Source) of three different molecular weights (Table 1), used as received. The complexes were prepared in a 1 : 3 molar ratio of the azobenzene relative to the pyridine units by dissolving the constituents separately in *N*,*N*-dimethylformamide, filtering the mother solutions through 200 nm syringe filters, and then mixing the two solutions. The 1 : 3 mixing ratio was chosen based on our previous work[31,32] as it combines high SRG formation efficiency and high film quality due to lack of chromophore–chromophore intermolecular interactions. The existence of phenol–pyridine hydrogen bonding in the complexes was verified by FTIR spectroscopy. The 993 cm^{-1} band of the free pyridine in pure P4VP was observed to shift to 1008 cm^{-1} in the complexes due to hydrogen bonding,[33] although, since nominally only one third of the pyridine groups are complexed, the 993 cm^{-1} band also remained present. A poly(Disperse Red 1 acrylate) (pDR1a) polymer of molecular weight 4300 g mol^{-1} was obtained from Sigma Aldrich and used as received.

Table 1 Molecular weight characteristics and glass transition temperatures of the polymers and the corresponding polymer–azobenzene complexes, compared with a covalent side-chain polymer, pDR1a, reported in the literature

Polymer	M_n (g mol^{-1})	PDI	T_g (°C)	Complex T_g (°C)
P4VP	1000	1.20	61	56
P4VP	3200	1.20	87	69[a]
P4VP	7000	1.04	126	90
pDR1a[36]	3700	N/A	95–97	

[a] T_g estimated by linear interpolation from the two other values, in the light of the T_g's for 0.25 complexes shown in Fig. S1 (ESI).

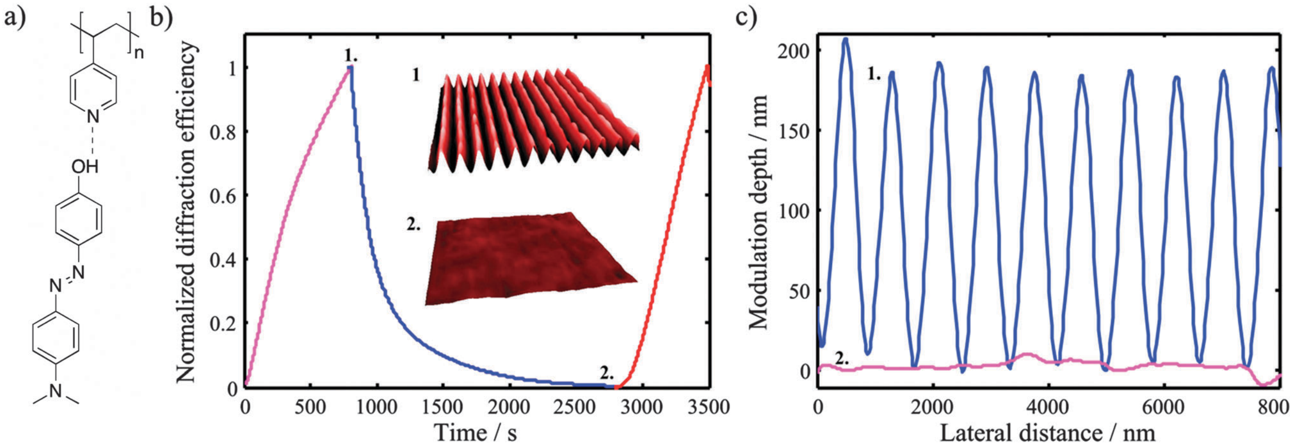

Fig. 1 (a) The chemical structure of the hydrogen-bonded P4VP–azobenzene complex used in this study. (b) Normalized first-order diffraction efficiency of the SRG inscription (magenta), erasure (blue) and rewriting (red) for the lowest molecular weight complex (1000 g mol^{-1}). The inset shows 3D AFM images of the inscribed SRG (1) and the film surface after SRG erasure (2). (c) AFM surface profiles before (1) and after (2) the optical erasure.

Thin film samples were prepared by spin-coating the complex solutions onto clean microscope slides (washed by successive sonication in acetone, isopropanol, and deionized water), followed by drying at 80 °C overnight. The resulting film thicknesses were *ca.* 200 nm. Samples to determine glass transition temperatures were prepared by dissolving the dry pure polymer and the complexes in THF and drop-casting in DSC pans. These pans were further vacuum-dried for 24 hours at room temperature. Measurements were made with a TA Instruments Q2000 calorimeter calibrated with an indium standard. The reported T_g's are averages of the inflection points of second and third heating scans made at 10 °C min^{-1}.

SRGs with a period of 800 nm were inscribed to a fixed depth of 180 nm (as verified by atomic force microscopy) using a 488 nm line of an Ar$^+$-laser and the Lloyd's mirror interferometer configuration for producing light interference patterns. The erasure was performed with a normally incident uniform laser beam from the same source. Both the inscription and the erasure of the patterns were carried out with 300 mW cm^{-2} irradiation intensity and horizontal polarization (unless otherwise stated), and the process was monitored by recording the 1st-order diffraction of a horizontally polarized 635 nm diode laser beam from the patterned surface. Atomic force microscopy (AFM) images were taken with a Veeco Dimension 5000 microscope in tapping mode. SEM images were taken with a JEOL FE-SEM JSM-7500FA after sputtering the sample surface with Au–Pd for 10 s.

Results and discussion

The material chosen for this study, shown in Fig. 1a, is known to produce high-quality SRGs relatively efficiently even at moderate or very low azobenzene concentrations.[31,32] The T_g's of the polymers (oligomers) and complexes are given in Table 1. As expected from the low molecular weights involved, which are well below the critical entanglement molecular weight (which, for P4VP, must be similar to that of polystyrene), the T_g's of both P4VP oligomers and P4VP–azobenzene complexes increase significantly with increasing molecular weight. Relative to pure P4VP, the T_g's of the complexes show a significant plasticization effect, as is common for hydrogen-bonded (and other) side-chain complexes, the extent of the effect being highly dependent on the material system.[34,35] In the present case, the plasticization effect increases with molecular weight, being only 5 °C for the complex of 1000 g mol^{-1} and 36 °C for the complex of 7000 g mol^{-1}. This can be understood considering that the hypothetical T_g of the azobenzene molecule used is likely to be only a little below that of the lowest molecular weight P4VP.

The 1st-order diffraction efficiency of a writing–erasure–rewriting sequence on a film of the lowest molecular weight complex (1000 g mol^{-1}) is presented in Fig. 1b. First, there is the diffraction build-up (0–800 s) resulting in a grating with a final modulation depth of 180 nm, as verified by AFM (3D image shown in the inset, with a cross-sectional profile given in Fig. 1c). At 800 s, the grating was exposed to a single Gaussian beam of linearly polarized light (polarization parallel to the grating grooves) with the same intensity and wavelength as during the inscription. After *ca.* 30 min of irradiation, the diffraction had vanished and no periodic surface modulation could be detected in the surface profile (Fig. 1c) of the AFM image (inset in Fig. 1b). To the best of our knowledge, this is a significant improvement of the state-of-the-art of optical erasure of deep surface undulations in amorphous polymeric materials below their T_g, since, thus far, optical erasure of SRGs of this depth range below the T_g has been incomplete.[20,21] Clearly, significant inverse mass transport (as compared to SRG formation) of the oligomer chains upon uniform illumination takes place during optical erasure. After this erasure, another SRG can be rewritten with equal diffraction efficiency on the same spot, as also shown in Fig. 1b.

Fig. 2a illustrates that the SRG formation efficiency increases drastically with decreasing molecular weight of the oligomer backbone, with the build-up of the first-order diffraction clearly being the fastest for the lowest-molecular-weight complex (1000 g mol^{-1}) and much slower for the highest-molecular-weight complex (7000 g mol^{-1}). (The full SRG inscription curves, where the highest diffraction efficiency reached is the same for the three complexes, thus giving gratings with a fixed depth of about 180 nm, are presented in Fig. S2, ESI.†) In this comparison, it should be noted that supramolecular complexation allows tracing the effect of molecular weight on the SRG formation without ambiguity, as the concentration of the azobenzene

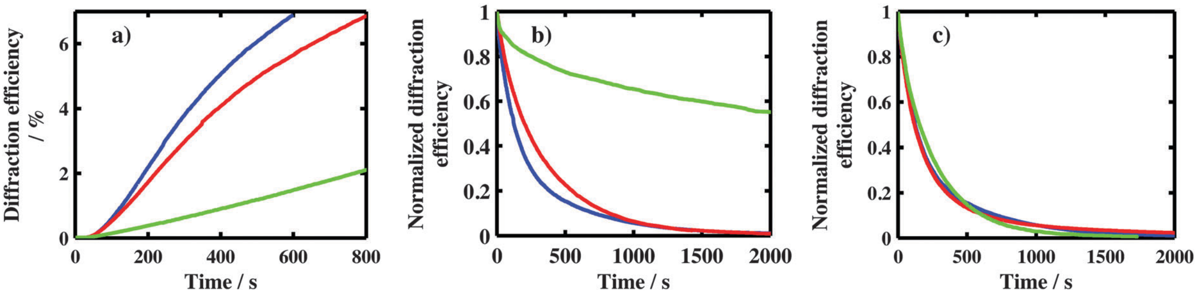

Fig. 2 (a) First-order diffraction efficiency upon SRG inscription on samples with oligomer backbone molecular weights of 1000 (blue), 3200 (red), and 7000 (green) g mol^{-1}. Normalized first-order diffraction efficiency upon photoinduced erasure (b) for samples with molecular weights of 1000 (blue), 3200 (red) and 7000 (green) g mol^{-1} and (c) for a sample of 1000 g mol^{-1} under erasure beam polarizations that are perpendicular (green) and parallel (blue) to the grating grooves, and under circularly-polarized irradiation (red).

units and the film thickness can be exactly controlled for each sample.

The negative molecular weight dependence of the surface patterning efficiency, which is well known and is related to the significant molecular weight dependence of the T_g and thus mobility of the molecules in the oligomeric M_w range,[37–39] motivated us to determine the effect of the molecular weight on the extent of optical SRG erasure. This is shown in Fig. 2b, which illustrates the normalized first-order diffraction efficiency upon erasure of these SRGs for the three molecular weights. Clearly, for the two lowest-molecular-weight complexes, for which the inscription process is fast, complete optical erasure is achieved, whereas for the highest molecular weight of 7000 g mol^{-1} the erasure is partial, at least within the 3600 s time span tested. Thus, not only SRG formation but also SRG erasure is dependent on the molecular weight of the migrating units and hence the T_g. This suggests that there is an optimal T_g range required for complete erasure, with the T_g of the 1000 and 3200 g mol^{-1} complexes (56–69 °C) falling within that range and the T_g of the 7000 g mol^{-1} complex (90 °C) being too high for complete optical erasure. These results are useful guides for the material designer, pointing towards the use of low molecular weight materials for efficient photoinduced surface patterning and erasure, at least at ambient temperature. It also calls for further investigations into the optical erasure of SRGs on molecular glasses, known to produce SRGs very efficiently.[40–43]

Previously, it has been shown that the mechanical changes upon illumination of an azopolymer leading to photo-induced flow are inherently different from mechanical changes induced by heating.[44] Since the T_g of the lowest molecular weight complex is 56 °C, which is about 30 °C above the operating temperature (as measured in the bulk; it may be different in thin films), and since the erasure wavelength used, 488 nm, is relatively far from the absorption maximum of the materials (shown in Fig. S3, ESI†) thus decreasing the efficiency of absorption-induced heating, it is highly unlikely that the process is driven by the heating of the material above its T_g by light absorption. In addition, using oligomeric materials below their critical entanglement point facilitates addressing the effect of the T_g on all-optical writing and erasing processes, and the present results show that, within the range studied, the maximum is reached with the lowest molecular weight and lowest T_g complex. It is thus tempting to conclude that the negative correlation with the T_g established for SRG writing[37] applies also to SRG erasure.

Lagugné-Labarthet *et al.* and Jiang *et al.* have reported on the strong dependence of the optical erasure of SRGs on the polarization of the erasing light.[20,21] The former observed that for poly(Disperse Red 1 methacrylate) (pDR1m), regardless of the polarization combination used to inscribe the gratings, the erasure rate constant is largest for linear polarization perpendicular to the grating grooves.[21] In contrast, the latter group found that, when erasing the gratings written with a polarization interference pattern created by right- and left-handed circularly polarized beams, linear polarization perpendicular to the grating grooves even increased the surface modulation by 44%.[20] They linked the observed polarization dependence to photo-orientation of azobenzene units upon illumination with polarized light.[20] Furthermore, Karageorgiev and co-workers demonstrated unambiguously that the photoinduced flow of pDR1m polymer is anisotropic in the direction of light polarization.[44] Motivated by these observations, we explored the effect of light polarization on the erasure dynamics, as shown in Fig. 2c. We found that the erasure process was essentially independent of polarization, and complete for all of the polarizations (two linear and one circular), as was further confirmed by AFM. Also, the polarization combination used to inscribe the SRGs did not affect the erasure behavior, unlike what was reported by Jiang and co-workers.[20]

However, when comparing the erasure behavior in the complexes to a commercially available poly(Disperse Red 1 acrylate) (pDR1a) polymer (molecular weight 4300 g mol^{-1}), which is comparable to the total M_w of the complex employing 3200 g mol^{-1} oligomer, we found that it was possible to only partially erase SRGs of similar depth to those in the complexes, 180 nm, as shown in Fig. S4 (ESI†). In this case, the erasure rate was dependent on the polarization, in agreement with the earlier studies on a similar material.[21] The significant differences in photo-orientation between the P4VP–azobenzene complexes of this study (photo-induced birefringence <0.02, $<50\%$ long-term stability[32]) and pDR1a (photo-induced birefringence *ca.* 0.1, $>80\%$ long-term stability[45]) may well explain the differences in polarization dependence of the erasure between these materials. Additionally, we note that the T_g may play a role in why complete optical erasure is not achieved in conventional DR1-based materials at any of the polarizations investigated. Specifically, as indicated in Table 1, the T_g of pDR1a is much higher than the complexes whose SRGs could be completely erased (M_n = 1000 and 3200) and similar to (or a little higher than, considering the slightly higher molecular weight of the pDR1a used here compared to the one in the Table 1) the T_g of the complex that was only partially erased (M_n = 7000).

Interestingly, in contrast to our results and to earlier results of partial optical erasure of azopolymer SRGs,[14,16,19–22] Yang and co-workers, and, recently, Sobolewska and co-workers have reported that SRG inscription can be enhanced when an additional monochromatic beam absorbed by the azopolymer impinges on the sample during the inscription process.[24,25] We tested this by applying a uniform linearly polarized beam of the same wavelength *in situ* during SRG writing (linear polarizations both parallel and perpendicular to the SRG grooves), which only led to deceleration in the SRG formation rate. This result can be interpreted as an interplay of simultaneous writing and erasure processes, and is in agreement with the independence of the optical erasure process from polarization. This divergence between the literature, reporting enhancement of the SRG inscription as well as unsuccessful and partial erasure attempts, and the complete optical erasure demonstrated here can be related to differences in molecular weight, photo-orientation and photoinduced mechanical changes in the materials, which may also be interrelated. First of all, the chemical structures and molecular weights of the various materials studied are different, resulting in very different T_g's.

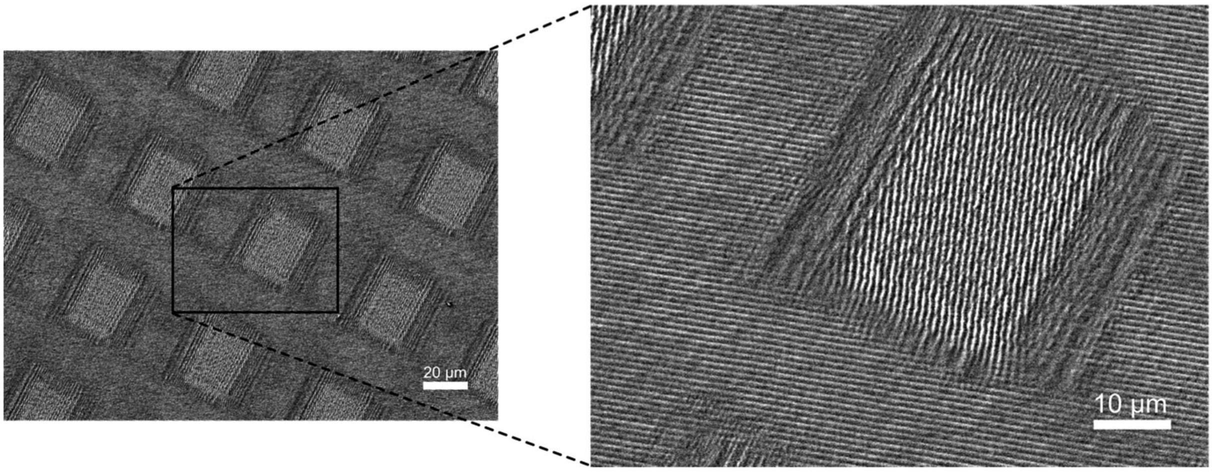

Fig. 3 Scanning electron microscopy images of surface patterns with spatially varying grating vector directions, created by first optically erasing the SRG in non-masked areas (where masking was accomplished by placing a transmission electron microscope grid onto a previously inscribed SRG) and then inscribing another SRG perpendicular to the original one through the mask.

As shown above, an increase in molecular weight with a concomitant increase in T_g results in a drastic deceleration of the grating erasure. Since ref. 19–21, demonstrating incomplete optical erasure, and ref. 24 and 25, demonstrating photoinduced enhancement of SRG inscription, do not provide data on the molecular weights or T_g's of their materials, further comparison to our results remains speculative.

On the other hand, differences in molecular weights and T_g's are insufficient to explain why, upon uniform illumination, there are only processes of decelerating SRG formation present in the materials used in this work, as opposed to enhancement in ref. 24 and 25. This points towards differences in photo-orientability, discussed earlier, together with polarization dependence, and photoinduced mechanical changes. Recently it was shown that hydrogen bonding may enhance photoinduced mechanical changes upon illumination with visible light as compared to covalent functionalization.[46] Along the same lines, in addition to the hindrance and directionality caused by stronger and more stable long-term photo-orientation, and a higher T_g, the extent of photoinduced mechanical changes in pDR1a may play a role in explaining the lower photo-erasure efficiency. From this point of view, the design of future materials that are capable of maximally transforming the mechanical changes into movement of the polymer backbone may benefit from the rigid spacer-less design explored in the current hydrogen-bonded complex.

Finally, in contrast to SRG erasure by heating the patterned film above the glass transition of the material[3,13] and in contrast to directly writing a second SRG on top of the film leading to a superposition of the two grating structures,[47] optical erasure allows for spatially controlled, selective removal of the surface pattern at ambient conditions, at the same time accentuating the fact that optical and thermal erasing processes are inherently different. To demonstrate the spatially selective patterning, we placed a transmission electron microscopy grid on top of an SRG to act as a mask to selectively erase the surface pattern from the non-masked areas, and then inscribed another pattern with a different grating vector direction onto the erased areas. Fig. 3 shows a scanning electron micrograph of a surface pattern prepared by this method. Clearly, with the proposed patterning method, precise spatially controlled surface patterning can be accomplished all-optically at ambient temperature.

Conclusions

We have shown that photoinduced surface-relief gratings with modulation depths of 180 nm inscribed in thin films of hydrogen-bonded oligomeric P4VP–azobenzene complexes can be completely optically erased with a single uniform beam below the T_g of the material, provided that the molecular weight of the oligomer is sufficiently low or that the T_g is not too high. The dynamics and extent of erasure do not depend significantly on light polarization, but only on the molecular weight of the migrating units. To the best of our knowledge, this is the first report showing that complete optical erasure depends drastically on the molecular weight, and thus the T_g, of the materials used. Since all-optical processing (both writing and erasing) can be done in ambient conditions, erasure of selected areas is also enabled, a clear advantage as compared to thermal erasure. This, combined with the fact that SRG inscription allows for tuning of both the grating period and the modulation depth over a wide range, paves the way for a variety of application possibilities. An additional advantage of the demonstrated erasure method is that it is not limited to grating patterns, but can be applied to any surface undulations. The proposed method of preparing high quality surface patterns with well-defined orientations thus highlights the versatility and applicability of azobenzene materials, amenable to all-optical control.

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