Holographic Recording in a Photoactive Elastomer**

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This work explores the use of photoactive elastomers as elastic holographic materials. Holographic gratings were recorded on stretched films of an azobenzene elastomer, which is composed of a side-chain liquid-crystalline polymer with azobenzene mesogens, grafted to the rubbery polybutadiene block of a styrene–butadiene–styrene (SBS) triblock copolymer. The grating-formation dynamics measurements revealed the formation of two gratings of different natures resulting from the coupled mechanical and optical effects. A first grating, formed quickly upon exposure, is due to the photoisomerization of oriented azobenzene groups. A second grating, developed at longer exposure times, may originate from changes in the anisotropic structure of the SBS matrix, which is induced by the photochemical phase transition of azobenzene mesogens. The first grating is unstable, but the second grating remains in relaxed films. Both mechanisms can be enhanced by deformation of the film.

1. Introduction

Photoactive polymers are promising materials for holographic recording having potential for data storage and optically configurable photonic device applications.[1–4] Generally, the chromophore used is either doped in a polymer matrix[3,4] or covalently bounded to the polymer.[1,2] Azobenzene-containing polymers are among the most studied photoactive polymers.[1,2,5–10] The reversible photoisomerization between the stretched trans and the bent cis isomers of the chromophore is the property exploited in all studies. When azobenzene polymers are used for holographic recording, a simple grating formation due to a periodic modulation of refractive index between disordered *trans*-and *cis*-azobenzene is not the most useful and efficient method, because of the small index difference. However, other mechanisms of grating formation have been discovered, particularly for two types of azobenzene polymers, which have proved to be very interesting. On the one hand, amorphous azobenzene polymers can be used to record prominent surface-relief gratings using an interference pattern.[11,12] Photoinduced mass transport on the surface of the polymer is believed to take place, even though the actual mechanism for the mass transport is still a subject of investigation.[13] On the other hand, liquid-crystalline azobenzene polymers turn out to be excellent for volume holographic gratings.[1,14] In this case, the large modulation of refractive index arises from a photochemical phase transition between the nematic state, which is compatible with the rod-like *trans*-azobenzene, and the isotropic state that contains disordered *cis*-azobenzene.

We have recently demonstrated a new type of azobenzene polymer, namely azobenzene elastomers.[15–17] As the unique feature of elastomers is the capability of undergoing large and reversible deformations, photoactive elastomers may be designed to couple the mechanical effects arising from deformation and the optical activity of the chromophore, which may lead to interesting functional properties. There are at least two utilities that are worth being exploited for elastic holographic materials: 1) using the deformation to enhance the diffraction efficiency, since the mechanism leading to the spatial modulation of refractive index may be amplified by deformation; and 2) adding the tunability to the holographic grating through reversible deformation of the film, as the deformation may dictate changes in the period of grating and the refractive index modulation depth. Reversible transition between different diffraction regimes (e.g., Raman–Nath and Bragg) can also be conceived with elastic holographic gratings. In our previous reports, in addition to the materials syntheses and studies of the coupled mechanical and optical effects,[15,17] we pointed out that diffraction gratings could be recorded on stretched films of the azobenzene elastomers by illumination through a photomask, and showed the mechanically tunable diffraction properties through simple film extension and retraction.[16] In the present work, we have investigated the use of the azobenzene elastomers as elastic holographic materials. The dynamic process of grating formation was monitored for films stretched to various extents in order to reveal the effects of deformation and to understand the mechanisms for the grating formation. As is shown below, the results suggest that the photoisomerization of azobenzene mesogens in stretched films may induce structural reorganizations in the polymer, leading to stable elastic gratings with high diffraction efficiency.

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2. Results and Discussion

The azobenzene elastomer, denoted as AE hereafter, was obtained by grafting a liquid-crystalline azobenzene polymer onto a styrene–butadiene–styrene (SBS) triblock copolymer.[15] Figure 1 shows its chemical structure and photos of the transparent AE and SBS films. The sample used in the present work contains about 8 wt.-% of the azobenzene polymer grafts. The elasticity of AE comes from the starting SBS polymer (30 % polystyrene), which is a thermoplastic elastomer in which the rubbery polybutadiene (PB) chains are interconnected by the glassy polystyrene (PS) cylindrical microdomains acting as the crosslink points.

Before reporting the results of holographic recording, it is useful to recapitulate the main features about the coupling of mechanical and optical effects on the mesogenic azobenzene groups in the AE films, which were revealed by a previous study.[15] This is schematically illustrated in Figure 2, where four different states of azobenzene groups in the film are depicted, and for each state two polarized UV-vis spectra of the film are shown (solid and dashed lines for polarization parallel and perpendicular to the strain direction, respectively). In the unstretched film, **1**, the elongated *trans*-azobenzene groups, whose absorption maximum is around 360 nm, are in the liquid-crystalline (LC) phase[18] but have no long-range orientation, as is seen from the spectra displaying no dichroism. If the unstretched film is exposed to UV light, the trans-to-cis isomerization occurs and the photochemical phase transition results in disordered *cis*-azobenzene groups (bent form), **2**, absorbing at about 450 nm and showing no dichroism. This process can be reversed by the cis-to-trans backisomerization of azobenzene either with visible irradiation or through thermal relaxation. From **1**, if the film is stretched, *trans*-azobenzene groups are aligned along the strain direction, **3**, resulting in the dichroism of the absorption peak. This mechanically induced orientation is enhanced by the liquid-crystallinity of the azobenzene polymer.[15] However, when the stretched film is illuminated with UV light, either polarized or unpolarized, the orientation of the *trans*-azobenzene groups is lost as they change to the

bent cis isomer,[15] **4**, which is revealed by the spectra. The situation in **4** can also be produced from **2**, i.e., stretching the film after UV irradiation. All the processes depicted in Figure 2 are reversible as indicated by the arrows; all changes in the opposing directions were observed experimentally. For the present study, holographic gratings were written on stretched films with oriented *trans*-azobenzene, **3**. Therefore, the grating a priori should be a grating whose spatial modulation of refractive index arises mainly from oriented *trans*-azobenzene in unreactive areas (dark fringes of the interference pattern) and disordered *cis*-azobenzene in reactive areas (bright fringes). It should be emphasized that the previous study[15] found that even when the stretched AE film is exposed to linearly polarized UV light, the only consequence is the conversion of *trans*-azobenzene to *cis*-azobenzene regardless of the polarization of irradiation light with respect to the strain direction. The absence of a photoinduced reorientation of the azobenzene groups in this polymer was mainly explained by a stable cis isomer.[15]

Figure 3 presents some results of grating-formation dynamics in films stretched to various strains; the recording beams were switched on at time = zero. Unless otherwise mentioned, the holograms obtained were in the Raman–Nath diffraction regime, the fringes were perpendicular to the strain direction and the polarization of the probe light was parallel to it. In this example, the period of grating is 2 µm and the power per pumping beam is 160 mW cm^{-2}. For comparison, the recording dynamics for an unstretched film are also shown. A grating is formed even in the unstretched film, which is thought to be due to the difference in refractive index between disordered *trans*-azobenzene and *cis*-azobenzene, i.e., between **1** and **2** in Figure 2. The diffraction efficiency η is, however, small because of the small modulation, and increases very slightly up to an exposure time of 300 s. When the film is stretched to a strain of only 20 %, η already displays a higher value, which shows the contribution from oriented azobenzene groups in the stretched film. Moreover, it is noticed that after a decrease following the peak value within the first 40 s exposure, the increase of η is more significant over time. These features become much more prominent with the film stretched to a strain
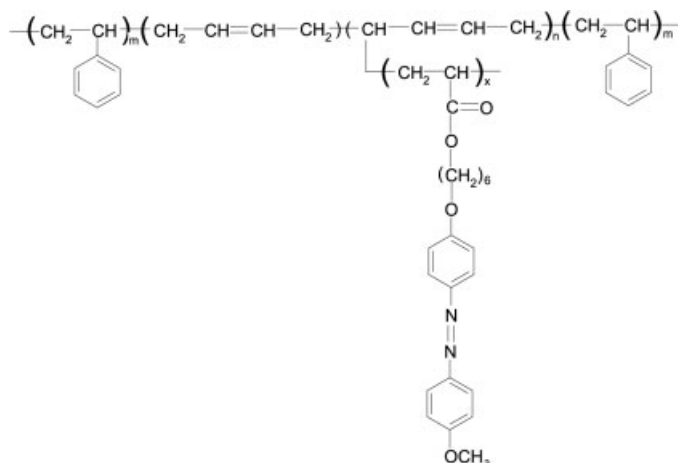

Fig. 1. Chemical structure of the azobenzene-grafted SBS polymer, with photographs showing transparent films of SBS (left band) and the orange-colored azobenzene elastomer (right band).
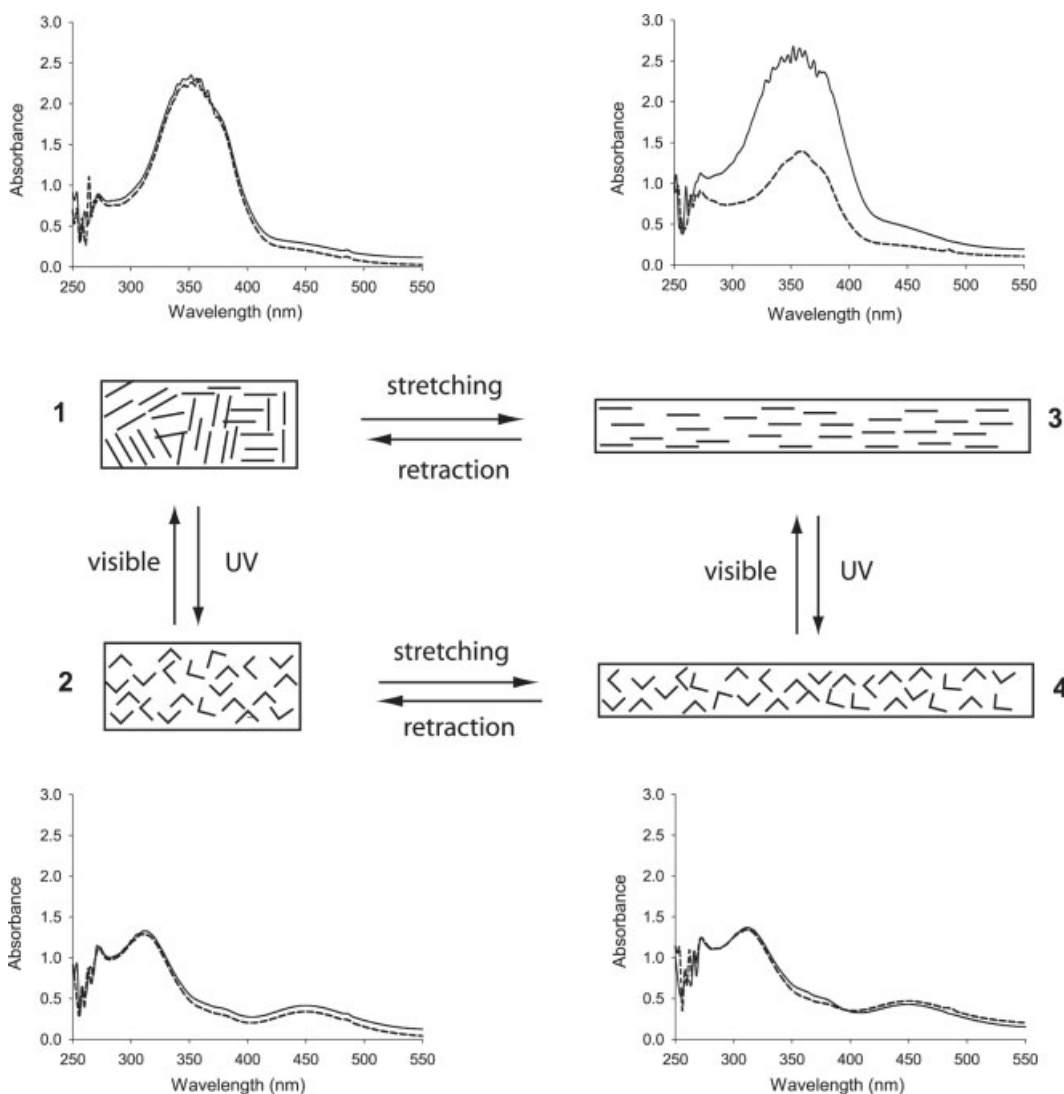
Fig. 2. Schematic and spectral illustration of the coupling of mechanical and optical effects on azobenzene mesogens in AE films. The polarized spectra were obtained with the beam of the spectrometer polarized parallel (solid lines) and perpendicular (dashed lines) to the strain direction. For the sake of clarity, only azobenzene mesogenic groups are depicted.
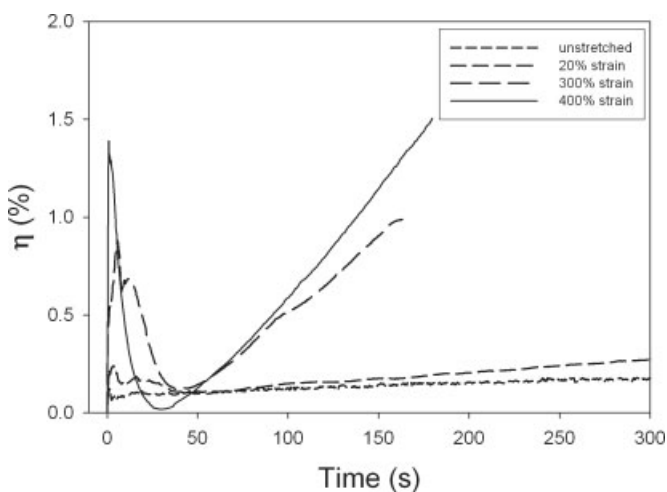

Fig. 3. First-order (+1) diffraction efficiency vs. exposure time for films stretched to various strains. The period of grating is 2 μm and the power per recording beam is 160 mW cm^{-2}.

of 300 %. At this large deformation, *trans*-azobenzene groups are well oriented[15] and the index mismatch, and thus the modulation depth, is more important, resulting in higher diffraction. However, this azobenzene grating appears unstable as η drops after about 20 s. Interestingly, another grating starts to develop at longer exposure times and η rises again. The effects of the film deformation on the grating formation dynamics continue to amplify with the film stretched to a strain of 400 %. These results show two phenomena: first, the deformation enhances the diffraction efficiency, and secondly, there are two grating-formation processes taking place in the course of exposure.

Additional experiments confirmed the different natures of the observed two gratings. Figure 4 shows an example in which the writing conditions are the same as in Figure 3 and the film was stretched to a strain of 400 %. Once the recording beams were turned on, the diffraction was observed as the grating was formed. But before the diffraction reached the transient peak,
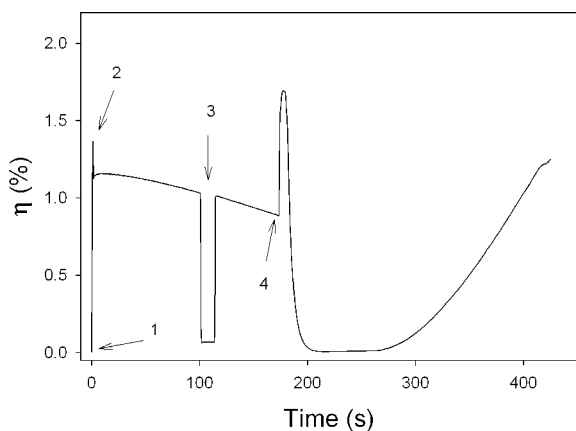
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Fig. 4. First-order diffraction efficiency vs. time for a film stretched to 400 % strain: 1) UV writing beams turned on, 2) writing beam turned off, 3) polarization of the probe light changed by 90° for 15 s, and 4) writing beam turned on again. The period of grating is 2 μm and the power per recording beam is 160 mW cm^{-2}.

the writing beams were turned off, which happened some 1.5 s after the writing started. The diffraction was then monitored for about 180 s. Over this period of time, without exposure, the grating was quite stable, showing a slight decrease in η, which may be caused by partial thermal relaxation of the *cis*-azobenzene groups. The sharp drop of η for about 15 s occurred when the polarization of the probe light was changed by 90° to be perpendicular to the strain direction (the initial polarization was re-established after the 15 s period). When the writing beams were turned on again, the diffraction rose again to complete the first process, and then dropped as the second process started. These results indicate that the grating formed quickly upon exposure comes mainly from, as expected, oriented *trans*-azobenzene and disordered *cis*-azobenzene groups, which is revealed by the strong dependence of η on the polarization of the probe light. It is easy to picture that when the polarization is parallel to the strain, the probe light feels the extraordinary refractive index of *trans*-azobenzene and the mean index of *cis*-azobenzene in the unreactive and reactive areas, respectively, and the difference is large. By contrast, when the polarization is perpendicular to the strain, the difference is now between the ordinary refractive index of *trans*-azobenzene and the mean index of *cis*-azobenzene, which is much smaller.[19] The erasure of the first grating seems to be caused by some structural perturbations arising from the photoisomerization of azobenzene mesogens. The development of a second grating formation process at longer exposure times is reminiscent of the formation of a surface relief grating in azobenzene polymers.[11–13] However, we checked the samples with atomic force microscopy (AFM), and found no surface relief grating. This is not really surprising because the used s–s polarization geometry for the two writing beams, whose vector of the electric field is parallel to the fringes, is known to be ineffective for inducing surface relief grating.[20] Therefore, the second process probably originates from some sort of structural reorganization in volume of the stretched films. The different nature of the second grating is also hinted at by the less important polarization dependence of the diffraction efficiency. For samples with a

well-developed second grating, changing the polarization of the probe light to be perpendicular to the strain decreases η by only about 30 %, in contrast with the 90 % drop in Figure 4 for the first grating.

Here, more discussions are necessary regarding the possible effects of a photoinduced reorientation of the azobenzene mesogenic groups on the formation of the second grating. For LC azobenzene polymers, the photoinduced reorientation is generally observed under polarized irradiation[21,22] and believed to be the origin of holographic gratings.[23,24] This, however, is unlikely to be the case for the AE films. As already mentioned earlier, our previous studies using polarized UV-vis and infrared spectroscopy clearly showed the absence of such photoinduced reorientation in stretched AE films.[15] A very slow thermally induced cis-to-trans backisomerization of the used azobenzene polymer was thought of as the main cause.[25] It is worth being mentioned that our recent investigations on diblock copolymers containing a LC azobenzene polymer revealed that the photoinduced orientation of azobenzene groups is severely reduced inside the constrained microdomain structures.[26] In the light of this finding, the particular morphology of the AE samples, with the azobenzene polymer grafts located in microdomains dispersed in the PB matrix, may also contribute to the prevention of the reorientation. Moreover, an analysis of other parameters also allows us to dismiss the possibility of any significant effect of the photoinduced reorientation, if there is any, on the formation of the second grating. On the one hand, with the used s–s polarization geometry the polarization of the interference pattern is perpendicular to the strain direction and the photoinduced orientation of azobenzene groups would be in the same direction as the stretch-induced orientation; consequently, no effective index modulation could be expected. On the other hand, unlike the LC azobenzene polymers used in most studies of holographic recording, the AE sample used in this work contains only 8 % of azobenzene polymer; even a strong reorientation of such a small amount of azobenzene groups could not account for the observed high diffraction efficiency shown below. Finally, there is a report on holographic gratings formed in an elastomer[27] due to photoinduced orientation of azobenzene chromophore, but the system is totally different because the azo dye used was doped in the polymer and the study involved no deformation of the elastomer. On the basis of the above analysis, a structural rearrangement initiated by the coupled mechanical and optical effects in the stretched AE films is most likely to be responsible for the second grating.

Before discussing the possible structural rearrangement in stretched AE films leading to the second grating, it is worth reporting a number of other experiments. Figure 5 shows the influence of the intensity of the writing beams on the recording dynamics on films stretched to a strain of 400 %, with a grating period of 5 μm. The powers per recording beam used were 40, 80, and 160 mW cm^{-2}, respectively. As the power increases, the erasure of the first azobenzene grating is faster and the second process starts more quickly. Using the film exposed to the 160 mW cm^{-2} recording beam, Figure 6 demonstrates that with long exposure time very high diffraction efficiencies can be
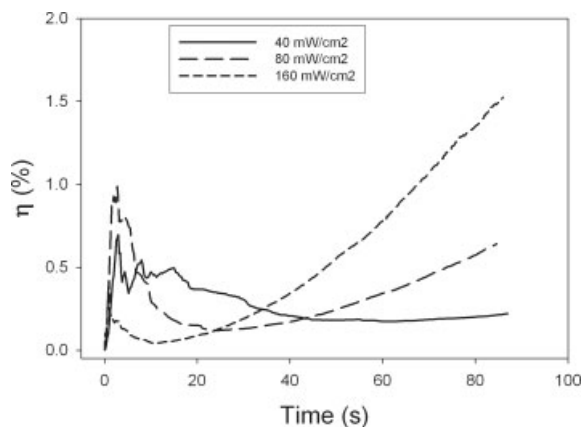
Fig. 5. First-order diffraction efficiency versus exposure time for films stretched to 400 % strain. The period of grating is 5 μm and the different intensities per recording beam are indicated in the figure.
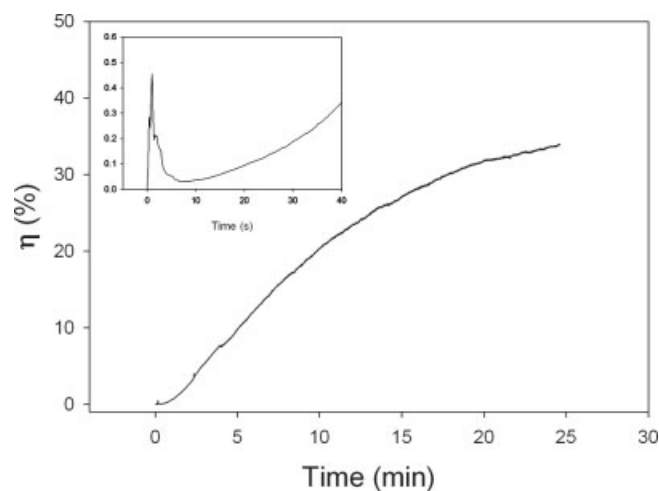

Fig. 6. Increase in diffraction efficiency with exposure time for the second grating recorded on a film stretched to 400 % strain. The inset shows the dynamic process of the first 40 s. The period of grating is 5 μm and the power per recording beam is 160 mW cm^{-2}.

achieved—over 30 % after 25 min. The inset in the figure shows the grating formation dynamics for the first 40 s. This strong index modulation depth is another indication that the second grating is unlikely to be originated from differences in orientation and/or conformation of the 8 % azobenzene polymer in the AE film. It would instead be formed through structural changes of the whole elastomer. In any event, if the azobenzene groups were the sole factor responsible for the second grating, the grating structure would disappear days after the holographic recording as a result of the thermally induced cis-to-trans backisomerization, which restores the equilibrium concentration of *trans*-azobenzene throughout the whole film. This is not the case, as Figure 7 shows the grating remained in the film used for Figure 6 seven months after the recording. During that period the film was stored in dark and in the relaxed state. As the initial grating had a period of 5 μm and was recorded on the film stretched to 400 % strain, the grating in the relaxed state has a period of 1 μm. The film shows no signs of degradation and remains highly elastic. Subsequent stretching
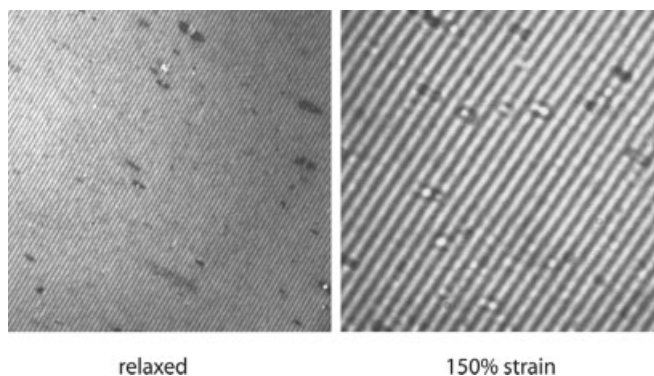

Fig. 7. Polarizing optical micrographs showing the grating remained in the film seven months after the recording. The period in the relaxed state is 1 μm, and it increases to 2.5 μm under a strain of 150 %. Micrograph area: 100 μm × 100 μm.

in the direction perpendicular to the fringes increases the period by an amount that is linearly proportional to the deformation, as can be seen from the example of 150 % strain that gives a period of 2.5 μm. Note that the stable grating on relaxed film could not be erased by UV or visible irradiation, which is another indication that azobenzene groups are not at the origin as discussed above.

The diffraction efficiency η of this remaining holographic grating was measured upon extension and retraction of the film. Summarized in Table 1 are the film length (measured between two ink marks for each step of stretching or retraction),

Table 1. The measured first-order diffraction efficiency of the grating in Figure 7 as a function of the film deformation. The data were used to calculate the refractive index modulation of the grating in Figure 8.

Film length, L [mm]	Draw ratio, Γ	Film thickness, d [μm]	η (extension) [%]	η (retraction) [%]
10[a]	1.0	26.0[b]	11.44	12.46
12	1.2	23.7	14.09	15.60
15	1.5	21.2	14.51	16.21
17	1.7	19.9	12.63	14.10
20	2.0	18.4	8.64	9.15
22	2.2	17.5	6.51	7.28
25	2.5	16.4	3.34	3.80
30	3.0	15.0	2.79	2.79

[a] The initial film length. [b] The initial film thickness.

the corresponding draw ratio $\Gamma = L/L_0$, where L_0 is the initial film length before deformation and L the film length at a deformation, and the measured η and the film thickness d at each deformation. The initial thickness before deformation $d_0 = 26$ μm was measured using a digital micrometer, whereas the change in thickness upon deformation was calculated according to $d = d_0\Gamma^{-0.5}$, which is valid for elastomers,[28] in order to not alter or break the film during the optical measurements. The data in Table 1 show that η changes in a reversible fashion within experimental error; it increases slightly with the deformation up to a strain of about 50 %, i.e., $\Gamma = 1.5$, and then decreases at larger strains. Since only the diffraction in the Raman–Nath regime was observed, we estimated the modulation of refractive index of the grating, Δn, from $\eta \approx (\pi d\Delta n/\lambda)^2$,[14] where λ is the wavelength of the probe light. Taking $\lambda = 633$ nm

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and $d_0 = 26$ μm, this equation gives to $\Delta n = 7.75 \times 10^{-3} (\eta \Gamma)^{0.5}$. From the data in Table 1, Δn at all deformations was calculated, and the results are shown in Figure 8, together with the plots of η versus Γ for comparison. Qualitatively, η changes in a similar way to Δn with deformation of the film, indicating that
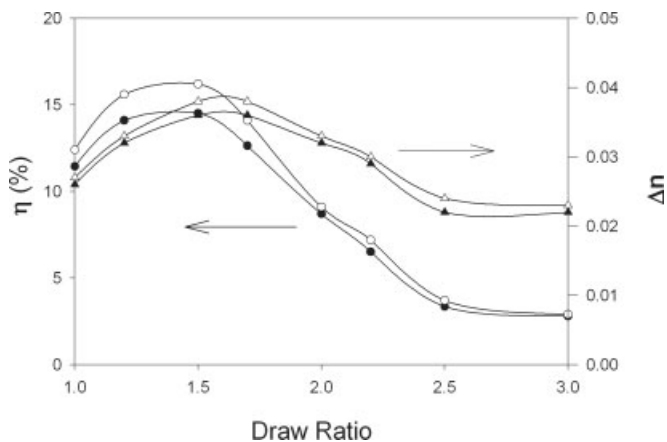

Fig. 8. Changes in both diffraction efficiency and modulation of refractive index as a function of draw ratio, for the grating remained in the film seven months after the recording (sample from Fig. 7).

the change in η is partly determined by the change in Δn. However, at high strains of $\Gamma \geq 2.5$, the sharp decrease in η is probably caused by the further decrease in the film thickness, because the change in Δn is much smaller.

Let us consider now the structural rearrangement in the AE films that could be responsible for the formation of the second holographic grating. To try to answer this question, we start the analysis with SBS, which is an well-studied thermoplastic elastomer. It is known that with about 20–30 % PS, the microphase-separated PS cylindrical domains play the role of cross-links, and that under high strain the oriented PB chains are supported by the PS cylinders that are aligned themselves at an angle to the strain direction. The works of Hashimoto and co-workers[29,30] have shown that when a highly stretched SBS film is annealed even at temperatures below the glass transition temperature T_g of the PS microdomains (~ 70 °C), plastic flow of PS chains may take place at the interface, which results in a relaxation of oriented PB chains and a change in the alignment of the PS cylinders as well. This thermally induced structural rearrangement in stretched SBS is more important with increasing the annealing temperature, which reduces the activation energy for the plastic flow of PS chains. The consequence of the PB orientation relaxation is a loss in the elasticity of the film (the film cannot recover to its initial length after removal of the stress), and the extent of this orientation relaxation can be qualitatively measured by the residual deformation of the film in the relaxed state. For stretched AE films that contain more than 90 % SBS, we believe that the formation of the second grating originates from a similar orientational relaxation of the PB chains, which is induced by an isothermal photochemical phase transition[31,32] from oriented *trans*-azobenzene to disordered *cis*-azobenzene.

The AE sample contains some 8 % azobenzene polymer grafts chemically connected to the PB chains, and the azobenzene polymer would form microdomains embedded in the PB matrix.[15] In a stretched AE film, in addition to the glassy PS cylindrical microdomains, the LC azobenzene microdomains may also act as cross-links and support part of the extensional stress. When the writing UV laser is turned on, the photoisomerization in the excited (reactive) areas converts oriented *trans*-azobenzene into disordered *cis*-azobenzene, which actually corresponds to an isothermal photochemical phase transition from the LC phase to the isotropic phase. As the azobenzene polymer in the isotropic phase is more fluid than in the LC state,[33] its microdomains are no longer effective as cross-linking points and, consequently, relaxation of oriented PB chains may occur, releasing the stress. As this happens, the stress is no longer uniformly distributed in space as before irradiation, and local structural reorganization may follow to rebalance the stress along the strain direction. This might be enough to disorder *trans*-azobenzene groups in the non-excited areas, which explains the erasure of the first grating. As the irradiation continues, the excited areas may undergo further structural changes due to the photoinduced isotropic state of the azobenzene polymer. That is, similar to the effect of thermal annealing at higher temperatures, in the optically plasticized areas, i.e., excited areas, greater plastic flow of PS chains takes place, which results in greater PB orientation relaxation and rearrangement of the PS cylindrical domains. The formation dynamics of the second grating, arising from such structural changes, should be slow and dependent on the power of the writing beam, which indeed is the case.

Unfortunately, polarized infrared spectroscopy could not be used to monitor the PB orientation in stretched AE films because of the overlapping of the absorption bands of SBS with those of the azobenzene LC polymer. However, the suggested light-enhanced PB orientation relaxation, triggered by the photochemical phase transition of the azobenzene polymer, was qualitatively confirmed by a simple experiment. When a film was irradiated under 400 % strain for 30 min, the residual deformation after removal of the stress, i.e., the loss of elasticity, increased by more than 50 % as compared to films subjected to the same treatment without irradiation. We tried to record a holographic grating on a pure SBS film stretched to 400 % strain; no grating was observed with the highest pump power used in this study (160 mW cm^{-2} per beam), indicating that the photochemical phase transition is necessary for the second grating-formation process. In principle, the index modulation depth of the second grating could come from three contributions: different PB chain orientations, different arrangements of PS cylindrical microdomains, or different azobenzene conformations and alignments. It has been shown from birefringence[30] and infrared dichroism measurements[34] that residual PB chain orientation exists in relaxed SBS films. Therefore, in a relaxed AE film after writing of the second grating, different residual PB orientations and different arrangements for PS cylindrical domains may exist in the excited and non-excited areas. The form birefringence of SBS

with 29 % of PS and perfect oriented cylindrical domains is about 6×10^{-4}.[30] The AE film discussed in Figure 8, which had a persistent grating in the relaxed state seven months after the recording, has a much greater refractive index modulation ($\Delta n = 0.026$). This implies that different residual PB chain orientations in the excited and non-excited areas could be the primary factor for the stable grating in the relaxed film. When the film is stretched, the index modulation depth may actually increase at modest strains, since different arrangements of PS cylindrical domains (anisotropic crosslink points) may lead to different PB chain orientations,[29,30,34] while under large strains the difference in PB chain orientation would become less important, resulting in a decrease in Δn. This would explain the results in Figure 8.

Finally, holographic gratings with a small period of 0.5 μm can also be written on stretched films. The diffraction may enter the Bragg (thick) regime, with the diffraction spot observed only at the resonance angle. Figure 9 shows the recording dynamics for a film stretched to a strain of 400 %; the
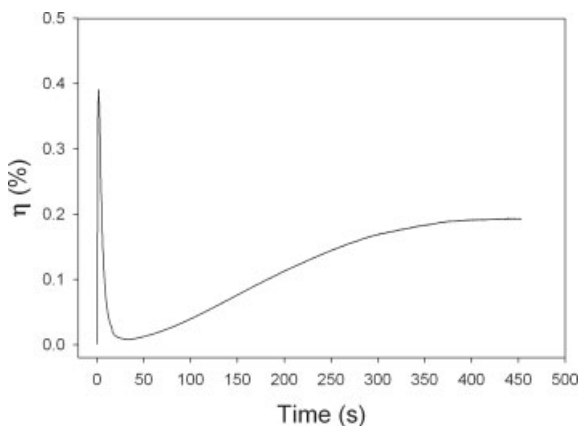
Fig. 9. Diffraction efficiency versus exposure time for a grating in the Bragg regime recorded on a film stretched to 400 % strain. The period of grating is 0.5 μm and the power per recording beam is 127 mW cm^{-2}.

power per recording beam was 127 mW cm^{-2}. Though the two grating-formation processes can still be seen, the diffraction efficiency becomes much smaller than in the Raman–Nath regime. In particular, the small period of 0.5 μm seems to approach the limit for the structural rearrangement to develop, leading to the low diffraction efficiency of the second grating. Indeed, as the grating period further decreases from 0.5 μm by relaxing the film, the diffraction becomes too small to be detected. Another interesting feature about the tunability of these elastic holographic gratings is the deformation-induced transition between the two diffraction regimes. We observed this phenomenon with a 1 μm period grating recorded on a stretched film (400 % strain). The grating was initially in the thin-film diffraction regime. As the film was relaxed, the period decreased while the film thickness increased, and the Bragg diffraction appeared in the relaxed film. The transition occurred over a range of deformations, in which both diffraction regimes were observed.

3. Conclusions

Photoactive elastomers are worth exploring as elastic holographic materials, for which the large and reversible deformation can be used to enhance the index modulation depth, to control the diffraction angle and to change the diffraction regime. In the case of the azobenzene-grafted SBS investigated in this work, holographic gratings recorded on stretched films are formed through two mechanisms due to the coupling of mechanical and optical effects. Photoinduced isomerization from oriented *trans*-azobenzene to disordered *cis*-azobenzene in excited areas is responsible for the first grating, which is formed quickly upon exposure but unstable, and also initiates the second grating formation process at longer exposure times. The second grating, with high diffraction efficiency and stability in the relaxed state, is believed to originate from enhanced orientation relaxation of the rubbery PB chains in the excited areas that are optically plasticized by the photochemical phase transition of the azobenzene mesogens.

4. Experimental

The AE sample used has a weight-average molar mass of 215 700 and a number-average molar mass of 108 000 (gas permeation chromatography (GPC) results using polystyrene standards). Thin AE films were prepared by casting a chloroform solution on the surface of a glass plate, and dried in a vacuum oven at 50 °C. After drying, the films were removed from the glass plate and kept in dark before use. The optical setup for recording holographic gratings is sketched in Figure 10. A Krypton UV laser ($\lambda = 350$ nm) was used for writing the gratings, and a He–Ne laser ($\lambda = 633$ nm) was used as the probe to measure the diffraction efficiency and to monitor the dynamics of grating formation. Gratings were re-

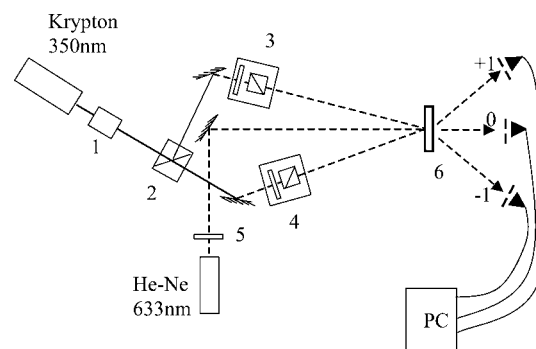Fig. 10. Sketch of the optical setup used for holographic recording: 1: beam expander; 2: beam splitter; 3,4: pairs of λ/2 and prism of Glan for the independent control of the polarizations and powers of two writing beams; 5: λ/2 for He–Ne laser; 6: sample.

corded on stretched films, which could easily be fixed on a glass slide using an adhesive tape, with the two pumping beams producing the interference pattern both linearly polarized perpendicular (s–s geometry) to the strain direction that is in the incidence plane, while the probe beam was polarized parallel to the strain of the film. The crossing angle of the two recording beams was adjusted to yield gratings with various periods. The power per recording beam with a diameter of 4 mm was measured using a power meter placed in front of the film. Photodiodes were utilized to measure the transmitted intensity, I_t, and the diffracted intensity (+1), I_d, of the probe beam simultaneously. The first-order diffraction efficiency (+1) was calculated as the ratio of I_d over I_t^0, where I_t^0 is the transmitted intensity before the writing of grating.

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