[29] It was not possible to measure the adsorption of DMAP stabilized gold nanoparticles onto bare (gold-coated) QCM electrodes, as the gold surface destabilized the nanoparticle solution and caused large $-\Delta F$ values, probably as a result of underpotential deposition.

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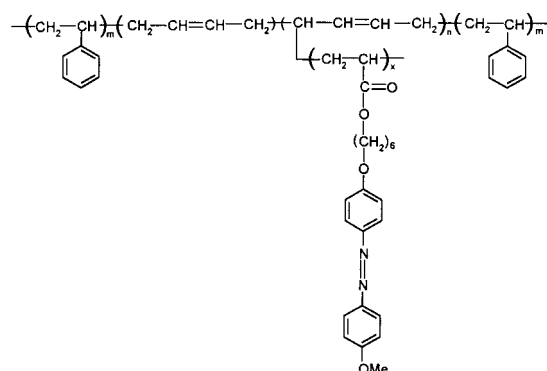[34] M. Brust, D. Bethell, D. J. Schiffrin, C. J. Kiely, *Adv. Mater.* **1995**, *7*, 795.

Mechanically Tunable Diffraction Gratings Recorded on an Azobenzene Elastomer**

By *Yue Zhao,** Shuying Bai, Dany Dumont*, and *Tigran V. Galstian*

Azobenzene-containing polymers have generated much interest because of their potential applications in holographic recording and other (e.g., guiding) photonic devices.[1–5] The efficient photoisomerization of azobenzene chromophores is at the origin of the attractive properties of these polymers. Studies reported so far have been focused mainly on two categories of azobenzene polymers: amorphous[4,5] and side-chain liquid crystalline polymers (SCLCPs).[1–3] An azobenzene polymer network has also been used to optically induce and stabilize the alignment of low-molar-mass liquid crystals.[6] Recently, we have grafted SCLCP-bearing azobenzene mesogens onto a styrene-butadiene-styrene (SBS) triblock copolymer.[7] The resultant material, referred to as AE hereafter, is an azobenzene thermoplastic elastomer, whose thin films can be prepared by solution casting, and reversibly stretched and retracted at room temperature. By coupling the mechanical and optical effects, an interesting phenomenon was revealed.[7] In essence, when a film of AE is stretched at room temperature, azobenzene mesogens are easily aligned in the strain direction because of the liquid crystallinity. Upon irradiation with polarized or unpolarized UV light, this orientation is erased as a result of the trans-to-cis photoisomerization, while on a subsequent irradiation with polarized or unpolarized visible light, the initial stretching-induced orientation is recovered due to the cis-to-trans back-isomerization. It was shown that this mechanism could be used to generate optical switching between orientation-on and orientation-off states. More interestingly, polarizing microscope observations

showed that stable gratings could be inscribed on stretched AE films. In this paper, we report on results that show reversible changes in the diffraction of light by gratings recorded on the AE films upon elastic extension or retraction. The study demonstrates the potential of exploring azobenzene elastomers as materials that may be used to make mechanically tunable optical or photonic devices.

The azobenzene elastomer AE has a basic chemical structure shown below[7]

The concentration of the azobenzene SCLCP ranges from about 10 to 20 wt.-%. Before grafting, the SBS triblock copolymer contains 30 % of polystyrene (PS). Similar to pure SBS, solution-cast AE films are elastic, and appear transparent and homogeneous. Considering the fact that the azobenzene SCLCP is immiscible with SBS, this observation implies that azobenzene grafts form microphases embedded in the rubbery polybutadiene matrix. The typical process employed to inscribe a grating is as follows. A stretched film was placed behind a photomask and exposed to UV light at $\lambda = 360$ nm; the irradiated areas lost the orientation of azobenzene mesogens due to photoisomerization, while non-irradiated areas retained the orientation. Afterwards, the film was relaxed to recover almost the initial length. It was found that the grating remained stable on the relaxed film at room temperature (some films show gratings recorded more than five months ago). The polarizing optical micrographs in Figure 1 show the interesting feature of such "elastic" gratings. On a film stretched to 300 % extension, i.e., a draw ratio of 4 (the draw ratio is defined as the film length after stretching over that before stretching), two gratings with 10 μm fringe spacing were written in parallel (left) or perpendicular (right) to the strain direction (photo a). The irradiated areas, including an uncovered region between the two photomasks, appear dark. The stretched film was then allowed to retract to its half-length (photo b); the fringe spacing of the perpendicular grating decreases, while it increases for the parallel one. (Note that one can easily find the Poisson coefficient relating the x, y, and z deformations of our elastomer). Gratings can be inscribed at any alignments, which result in different changes in fringe spacing upon elastic extension and retraction of the film. Moreover, these gratings are anisotropic and sensitive to their relative orientation to the crossed polarizers. The micrographs in Figure 1 were taken with the strain direction making

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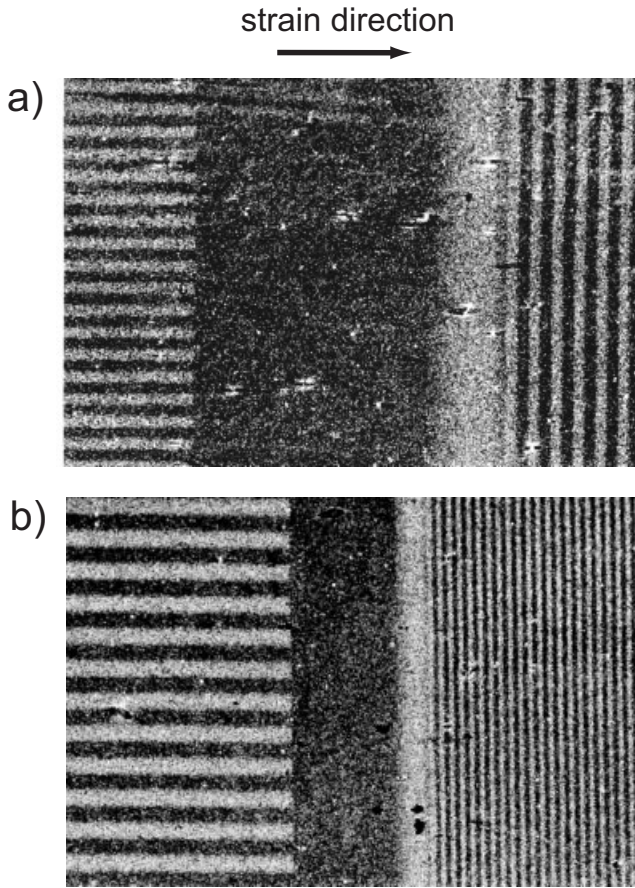Ste-Foy, Québec G1 K 7P4 (Canada)

strain direction

a)

b)

Fig. 1. Polarized optical micrographs for a) two gratings (10 μm fringe spacing) inscribed on an AE film stretched to 300 % extension, with their fringes parallel and perpendicular to the strain direction; and b) the two gratings on the same film retracted to the half-length.
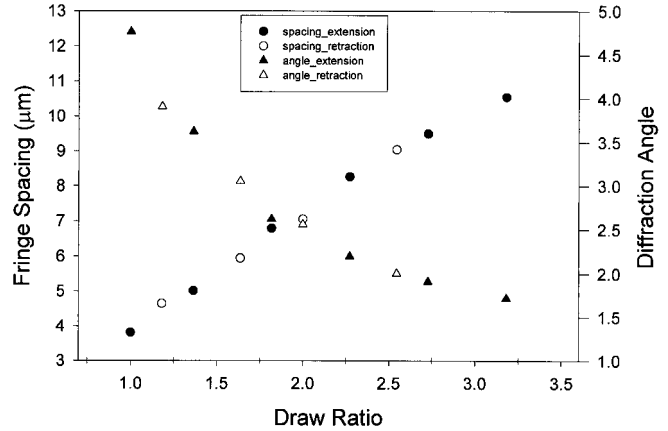

Fig. 2. First-order diffraction angle (triangles) and calculated fringe spacing (circles) vs. draw ratio for a grating inscribed on an AE film subjected to extension (closed symbols) and retraction (open symbols).
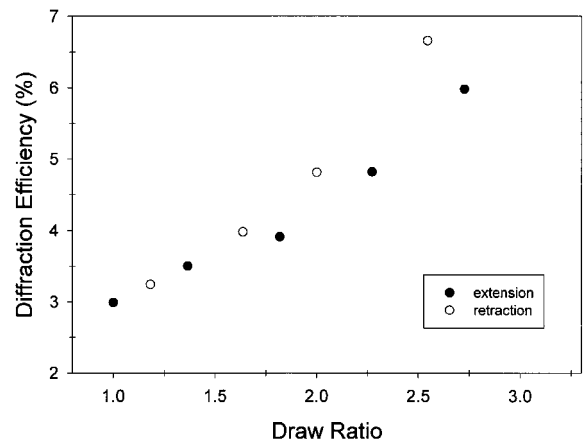

Fig. 3. First-order diffraction efficiency vs. draw ratio for a grating inscribed on an AE film subjected to extension (closed symbols) and retraction (open symbols).

a small angle (about 5°) to the polarizers, where the gratings are clearly visible. When the strain direction is parallel to the direction of the polarizers, the whole film shows extinction and the gratings can hardly be seen.

The first-order diffraction of light was measured using an AE film containing 10 % of azobenzene SCLCP grafts. The film was stretched to 300 % extension (it had a thickness of about 10 μm under strain); after inscription of a grating perpendicular to the strain direction, the film was relaxed. The measurements were carried out on the film that was fixed on a manually controlled stretching device and subjected to extension and retraction. Figure 2 shows both the measured diffraction angle, Θ, and the calculated fringe spacing, Λ, according to $\Lambda = \lambda/(2 \sin\Theta)$, as a function of draw ratio. It is clear that the fringe spacing changes linearly and reversibly upon elastic extension and retraction of the film, leading to reversible changes in the diffraction angle.

The diffraction efficiency was also measured as a function of draw ratio, and the results are shown in Figure 3. Taking into account the experimental uncertainties related to the measurements, data in Figure 3 seem to point out a quite reversible change in the diffraction efficiency upon extension and retraction of the film. It may be seen that the diffraction

by this type of grating is quite efficient and dependent upon the deformation of the film; the efficiency increases as the film is stretched up to about 170 % extension (no measurements could be made at larger deformations because of the diffraction angle becoming too small to place the two detectors side-by-side). This result indicates that differences between irradiated and non-irradiated areas are greater when the film is under a larger strain. On the other hand, it was found that the diffraction efficiency is highly polarization-sensitive. Figure 4 shows the plots of the diffraction efficiency vs. the polarization angle of the probe light for a film under a 150 % extension (draw ratio = 2.5) and at the completely relaxed state (draw ratio = 1). A polarization angle of 0° means that the polarization is parallel to the strain direction, which is horizontal. The diffraction efficiency changes in a similar way in both cases; it decreases as the angle between the polarization of the probe light and the strain direction increases. With respect to the grating, the maximum efficiency is found when the polarization is perpendicular to the fringes, while the minimum efficiency is observed when the polarization is parallel to the fringes. Errors on the data of diffraction efficiency were estimated to be below ±0.3 %.
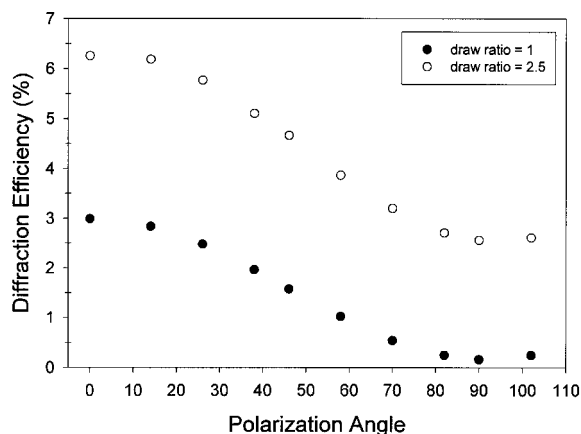
Fig. 4. First-order diffraction efficiency vs. polarization angle of the probe light for a grating inscribed on an AE film stretched to 150 % extension and in the completely retracted state.

In the completely relaxed state, as non-irradiated areas should be isotropic, the result in Figure 4 suggests that irradiated areas be anisotropic. The probe light senses a larger difference between reactive and non-reactive areas when the polarization is perpendicular to the fringes than when it is parallel. When a film is under strain, non-irradiated areas also become anisotropic because of the stretching-induced orientation of both polybutadiene (PB) chains and azobenzene mesogens. However, this orientation also enhances the anisotropy in the irradiated areas and, surprisingly, the polarization dependence remains the same as in the relaxed state, although the diffraction efficiency increases (Figs. 3 and 4). As already mentioned, a previous orientation study[7] found that irradiated areas lose the orientation of azobenzene mesogens upon UV exposure due to the trans-to-cis photoisomerization, which should initiate the formation of the grating. But when the film is relaxed, both irradiated and non-irradiated areas lose the orientation of azobenzene and, at room temperature, recover to the trans-rich state after about 10 h. Therefore, the stable grating observed in the relaxed film implies that some structural or morphological changes occurred during the photoisomerization of azobenzene in the irradiated area. This is not unlikely considering the fact that, under a highly stretched state, aligned azobenzene moieties are linked to the oriented, rubbery PB chains, which interconnect the PS cylindrical microdomains acting as the crosslinking points and supporting the mechanical force in this type of thermoplastic elastomer.[8,9] The randomization in the orientation of azobenzene moieties during the irradiation under strain may affect the orientation of the PB chains and induce a rearrangement of the PS cylinders. The mechanism remains unclear at this point and is the subject of our ongoing investigations.

This study shows the potential of exploring a new type of azobenzene polymers, namely azobenzene elastomers. In principle, one can envisage to implement the attractive properties known for azobenzene polymers, e.g., surface relief gratings,[4,5,10] on azobenzene elastomers. This implementation may result in new possibilities and perspectives in the search for functional materials because of the reversible elastic deformation. For instance,

if gratings with specific optical or photonic functions are made on azobenzene elastomers, these functions become mechanically tunable, and novel applications may be conceived.

Experimental

Details on the synthesis and characterization of AE were reported elsewhere [7]. Thin films were obtained by casting a chloroform solution onto the surface of a glass plate, followed by drying in vacuum. The thickness of the films was made to be about 10–12 μm under strain. Photomasks were used for inscription of the gratings. The UV exposure was conducted using a 1000 W Hg (Xe) lamp (Oriel) with filters; the actual irradiation intensity was about 2 mW cm^{-2} and the irradiation time was 10 min.

For the measurements of diffraction, a He–Ne laser operating at 632.8 nm was used. Its polarization was set and controlled using a Glan polarizer and a halfwave plate. Both transmitted and diffracted signals were detected using photodiodes at a large distance (0.8 m) from the AE film to avoid scattering noise and to measure the diffraction for large draw ratio of the film. The setting of the second detector was always done by lateral displacement and maximizing the measured intensity. The diffraction angle Θ was extracted from the ratio of the distance between the two signals over the distance from the film.

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Electric Field Tuning of the Stop Band in a Liquid-Crystal-Infiltrated Polymer Inverse Opal**

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Photonic crystals with a three-dimensionally ordered structure with periodicity of the optical wavelength have attracted considerable attention from both fundamental and practical

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