Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Viscoplastic photoalignment modeling of asymmetric surface restructuring in azopolymer films by elliptically polarized light

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I. Calculating the rotation of polarization azimuth

Here we review the rotation of the azimuth of an elliptically polarized light passing through an azopolymer due to self-induced linear birefringence. Differently from Nikolova et al.,[1] the recalculation is carried out in a right-handed reference frame, in order to assess the relation between ellipticity of the light and the rotation sense of the azimuth. Let us adopt the most common convention in optics for the handedness of light polarization,[2] according to which the polarization is *right-* (*left-*) handed if the endpoint of the electric-field vector ***E*** rotates in a *clockwise* (*anti-clockwise*) sense when looking *against* the direction of propagation of the beam. Here we consider the elliptical polarization

$$E_{in} = R(\beta_0)\begin{bmatrix} a \\ i\ b \end{bmatrix} = \begin{bmatrix} \cos\beta_0 & -\sin\beta_0 \\ \sin\beta_0 & \cos\beta_0 \end{bmatrix}\begin{bmatrix} \cos\varepsilon \\ i\ \sin\varepsilon \end{bmatrix} \quad \text{(S1)}$$

where $a > b$ are the semi-major and semi-minor axes, $e \equiv b/a$ is the ellipticity, $\varepsilon \equiv \tan^{-1}(e)$ the ellipticity angle and β_0 the azimuth of the elliptical polarization before entering the sample (*right* handed in Figure 2a). Following the Weigert's effect, azo-chromophores reorient perpendicular to the major axis *a* of the ellipse, thus inducing a negative birefringence $\Delta n \equiv n_{\parallel} - n_{\perp} < 0$. Its value is function of the ellipticity angle ε

$$\Delta n = \Delta n_0\,(\cos^2\varepsilon - \sin^2\varepsilon) \qquad \text{(S2)}$$

where Δn_0 is the maximum birefringence induced by the linearly polarized light beam (i.e. $\varepsilon = 0$). The Jones matrix which describes the propagation of the first thin (Δz) layer at the entrance surface of the azopolymer film is

$$T(0,\Delta z) = R(\beta_0)\begin{bmatrix} \exp\left(-i\,\frac{2\pi}{\lambda}n_{\parallel}\Delta z\right) & 0 \\ 0 & \exp\left(-i\,\frac{2\pi}{\lambda}n_{\perp}\Delta z\right) \end{bmatrix} =$$

$$R(\beta_0)\exp\left(-i\,\frac{2\pi}{\lambda}\bar{n}\Delta z\right)\begin{bmatrix} \exp\left(-i\,\Gamma_{\Delta z}\right) & 0 \\ 0 & \exp\left(i\,\Gamma_{\Delta z}\right) \end{bmatrix} \quad \text{(S3)}$$

where $\bar{n} \equiv (n_{\parallel} + n_{\perp})/2$ is the average refractive index and $\Gamma_{\Delta z} \equiv \pi\,\Delta n\,\Delta z/\lambda$ the half-phase retardation between the extraordinary and ordinary waves due to the propagation depth Δz.

Following the same procedure adopted in Ref. [1], one can calculate the rotation of the azimuth $\Delta\beta \equiv \beta(z,\varepsilon) - \beta_0$ experienced by the beam when it propagates by a distance *z* into the photobirefringent film:

$$\Delta\beta(z,\varepsilon) = 2\Gamma_z \frac{e}{e^2-1} = -\frac{\pi\,\Delta n_0\,z}{\lambda}\sin 2\varepsilon \qquad \text{(S4)}$$

where $\Gamma_z \equiv \pi\,\Delta n\,z/\lambda$ is half-phase retardation at distance *z*.

According to Eq. (S4) and assuming $\Delta n_0 < 0$, the azimuth rotates *anti-clockwise* ($\Delta\beta > 0$) for *right*-handed polarization ($0 < \varepsilon \leq \pi/4$) and *clockwise* ($\Delta\beta < 0$) for *left*-handed polarization ($-\pi/4 \leq \varepsilon < 0$), looking against the direction of propagation of the beam, which is in contrast with the conclusion in in Ref. [1].

The dependence of the azimuth rotation in term of the half-phase difference δ between the interfering beams, reported in Eqs. (11) and (12) of the main text,

$$\Delta\beta(z,\delta) = \frac{\pi\,\Delta n_0\,z}{\lambda}\sin 2\delta \qquad \text{(S5)}$$

is obtained from (S4) by calculating[2]

$$\sin 2\varepsilon = \frac{2\, Im[\chi]}{1+|\chi|^2} = -\sin 2\delta. \qquad \text{(S6)}$$

Here $\chi \equiv E_y/E_x$ is the ratio between the y and x components of the Cartesian Jones vector of the interference fields $\tilde{E}_{OL}(\theta)$, described by Eq. (10) of the main text. Note that for consistency we use degrees in the main text, and therefore π in Eq. (S5) is swapped to $180°$ in Eq. (12) of the main text.

II. Details of ANSYS implementation

The modeling of grating inscription is done in the finite element software ANSYS. The sample is "glued" to the substrate by applying the fixed support to its bottom face. Four vertical faces are restricted from moving in the normal direction by application of frictionless support. To properly model viscoplastic deformations, the option "Large Deflection" is switched on. The light-induced stress tensor is implemented using the subroutine Userthstrain, as described elsewhere.[3-4] This subroutine generates the light-induced strains along the principal directions of stress tensor. These directions are chosen for each finite element in accordance with the applied polarization pattern.

In the absence of correction all polarization patterns are symmetric around $\delta = 90°$ and modeled gratings appear to be symmetric, see Figure S1a. This is because the light-induced strain along the grating direction, i.e. along the global x axis, is symmetric, see Figure S1b. It is compressive (negative) at positions of peaks and expansive (positive) at valley positions.

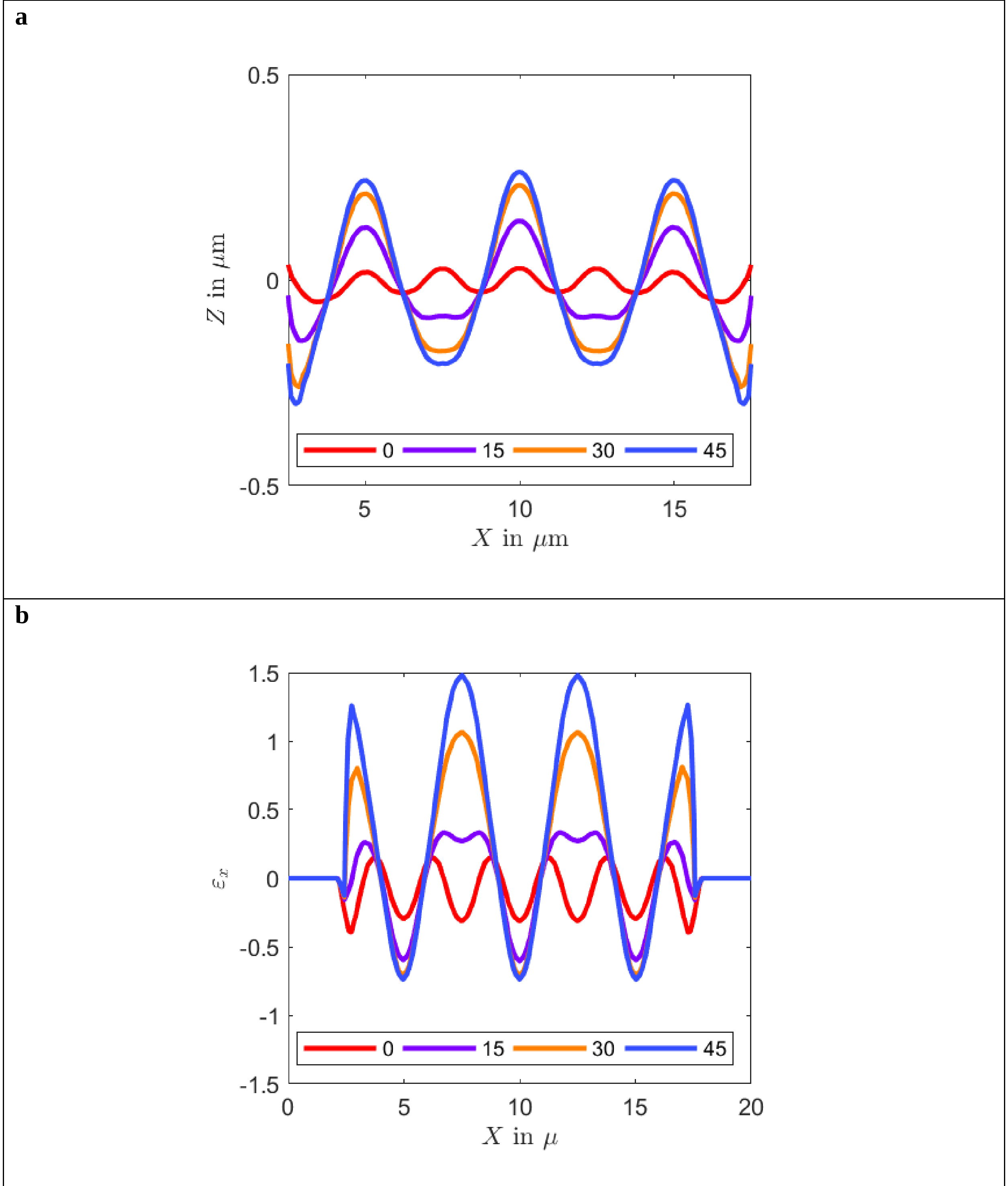

Figure S1. (a) Modeled height profiles taken along the central path of illuminated area at $y = 7.5\,\mu$m in the absence of self-induced light polarization rotation. (b) The light-induced strain along the x axis for uncorrected interference patterns.

Figure S2 shows the light-induced strain for the interference patterns corrected on the effect of self-induced light polarization rotation. It is clearly seen that the strain is only asymmetric at the angles $\theta = 15^{\circ}$ and $\theta = 30^{\circ}$.

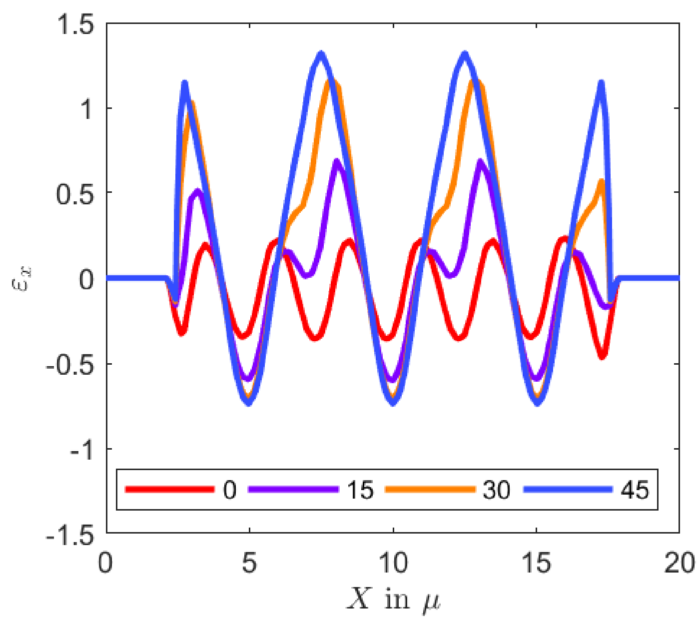

Figure S2. The light-induced strain along the x axis for corrected interference patterns.

The sample height is divided into $k = 4$ elements along the z axis. Each of these elements is characterized by its own azimuth rotation angle

$$\Delta\beta(z_i) = 180^{\circ}\Delta n_0 \frac{z_i}{\lambda} \sin 2\delta \qquad \text{(S7)}$$

calculated at the penetration depth $z_i = h/2k \cdot (2i-1)$, $i = 1..k$. Note that the depth is rescaled on the thickness of the film, $h = 6.4$ μm, used in the experiment of Pagliusi & co.[5] Interestingly, the modeling results hardly change, see Figure S3, when instead of Eq. (S7) the azimuth rotation angle, averaged over the film thickness h, is applied to all k-elements:

$$\Delta\beta_{av} = 180°\Delta n_0 \frac{h}{2\lambda}\sin 2\delta . \tag{S8}$$

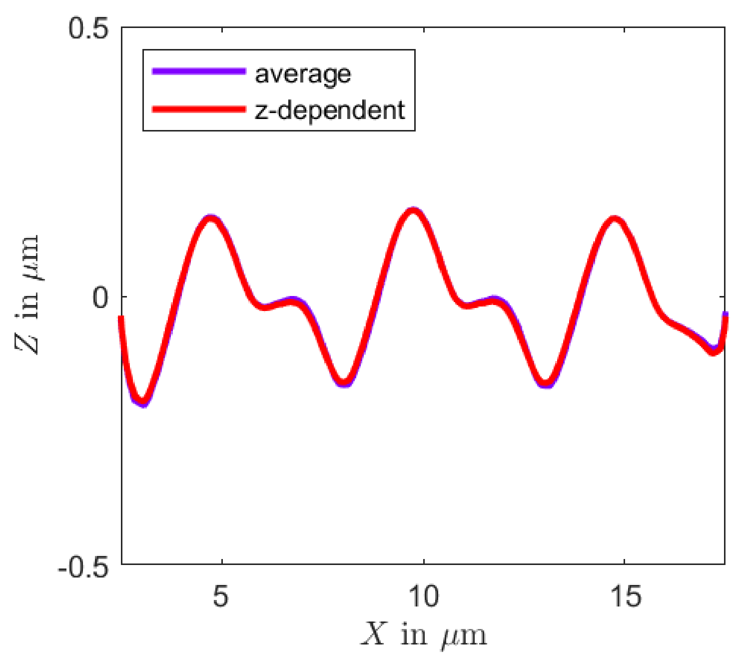

Figure S3. Height profile (red line) inscribed by the interference pattern with $\theta = 15°$ corrected on the z-dependent angle of light-induced polarization rotation (S7). It does not differ from the height profile (violet line) inscribed by the interference pattern corrected on the average angle of light-induced polarization rotation (S8).

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