Supporting information

How to choose for spontaneous patterning between molecular cooperation or non-cooperation?

Lina Zang,[1] Regis Barille,[1*] Sonia Zielinska,[2] Aleksandra Korbut,[2] Ewelina Ortyl[2]
[1]Univ Angers, CNRS, MOLTECH-ANJOU, SFR MATRIX, F-49000 Angers, (France)
[2]Department of Polymer Engineering and Technology, Wroclaw University of Technology, Faculty of Chemistry, 50-370 Wroclaw, (Poland)

Material

Samples are polymer films made from a highly photoactive azobenzene derivative containing heterocyclic sulfonamide moieties: 3-[{4-[(E)-(4-{[(2,6-dimethylpyrimidin-4-yl) amino] sulfonyl}phenyl) diazenyl]phenyl}-(methyl)amino]propyl 2-methylacrylate [1]. Thin films on liquid substrates were prepared by dropping of the polymer from THF solutions with a concentration of 50 mg/ml. Thickness measured with a Dektak-6M Stylus Profiler was around 300 µm. The λ = 476.5 nm laser line of a continuous argon ion laser is used to excite the azo- polymer close to its 438 nm-absorption maximum. Absorbance at the working wavelength is 1.6.

[1] E. Ortyl, R. Janik, S. Kurcharski, 'Methylacrylate polymers with photochromic side chains containing heterocyclic sulfonamide substituted azobenzene,' Eur. Polymer J. 38, 1871- 79 (2002).

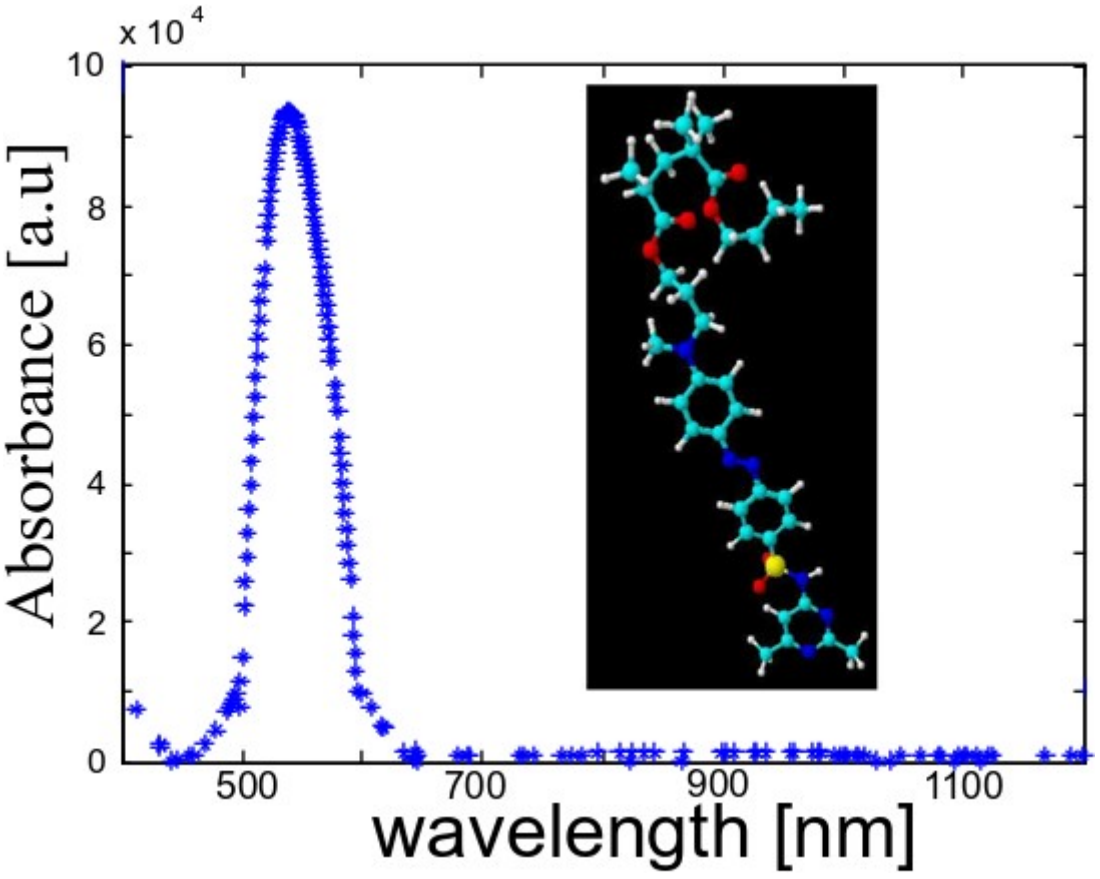

Fig. SI1: Absorption measurement of the azopolymer compound used for the fabrication of thin films.

Set-up

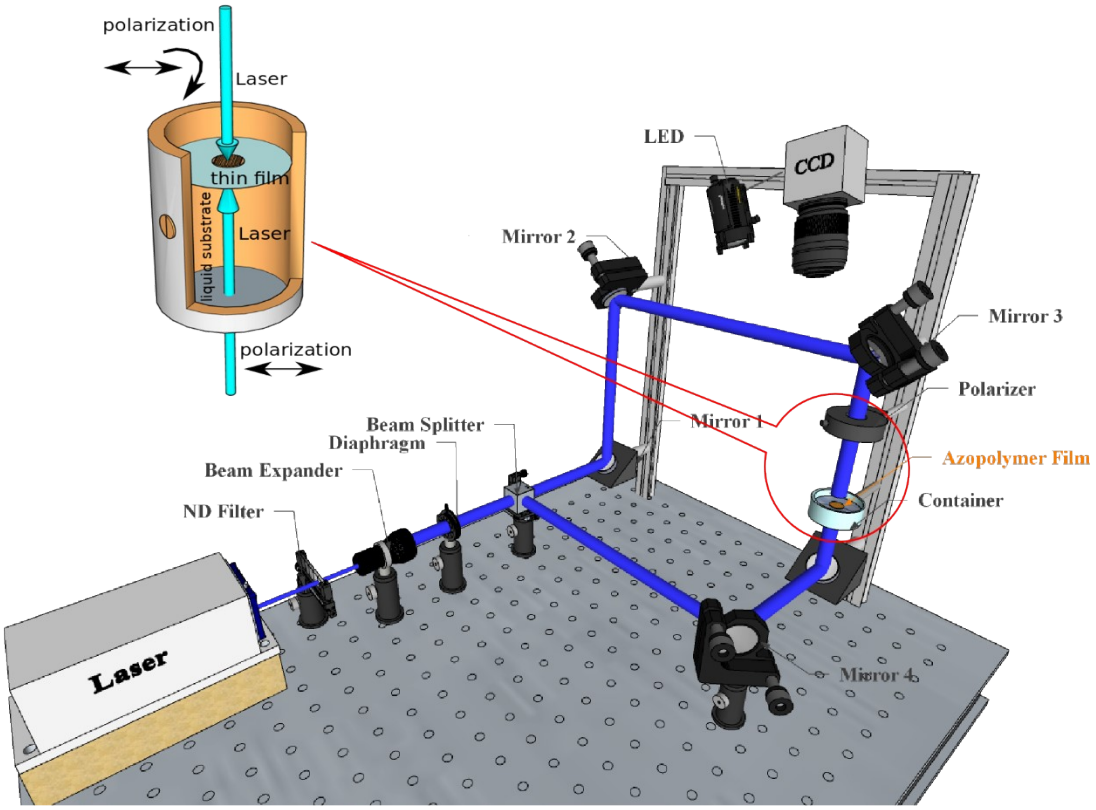

Fig. SI2: Set-up for the illumination of the thin film with two lights: 1) laser (fixed polarization) + laser (different polarization), 2) laser + laser (different intensity), 3) laser + white light.

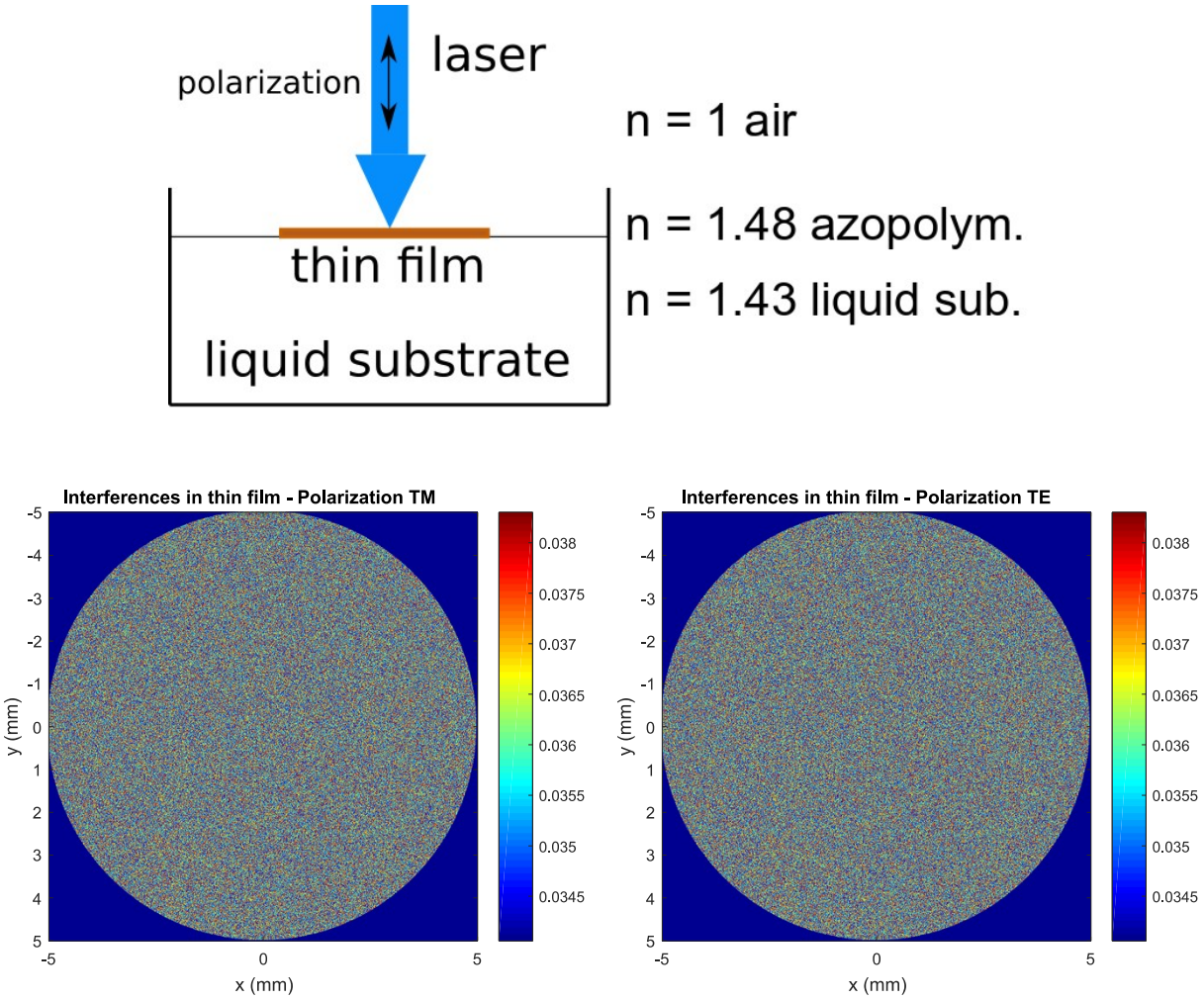

Fig. SI3: Simulation of the light reflected into the thin film of 200 µm when the thin film is illuminated with a beam diameter of 1 cm for two different polarization and a roughness of ± 10 µm.

Physical parameters:
- Wavelength: 473 nm (blue laser).
- Refractive indices: air ($n_o = 1$), thin film ($n_1 \approx 1.485$), substrate ($n_2 \approx 1.4385$).
- Average thin film thickness: 10 µm, with a random roughness of ±10 nm.
- Modelling of the laser beam as a circular surface 1 cm in diameter, sampled on a 1000×1000 grid.

Roughness simulation:
- Random roughness is generated: each point on the film has a small variation in thickness between ±10 nm.

Interference calculation:
Fresnel coefficients are calculated to model the reflection at each interface (air/film, film/substrate). The results show calculations of the optical phase through which light passes in the film, taking into account the local thickness, then it was deduced the effective reflection coefficient of the multilayer system. Finally, the reflected intensity was calculated as a function of position.
The results display an image of the distribution of the reflected intensity over the entire surface of the beam.
The result shows how the surface roughness and thickness of a thin film affects laser interference and reflection.

simulation

The general non-linear partial differential equation presented by H. Galinski et al is modified and includes terms for:

- a term governing the interaction between azopolymer under light irradiation,

- a diffusion term representing the mobility and the spatial distribution of the polymer chains,

- an external field term used to model the effects of and optical field. This external field is modelized with a Gaussian beam and an additional factor describing the laser coherence.

$$\frac{\partial u}{\partial t} = D\nabla^2 u + f(u, v) + g(x, y, t)$$

where $u(x,y,t)$ is the concentration of the azopolymer, D is the diffusion coefficient, $f(u,v)$ is the reaction term, and $g(x,y,t)$ is an optical field term.

The equation is then written to simulate the pattern illuminated by the two laser beam.

$$\frac{\partial c}{\partial t} = \alpha\Delta_{x,y}c + \Delta\big(-ec + gc^3 - \kappa\Delta c\big) - B(c - c_0)$$

where c_0 represents the reference or baseline concentration for the cis- and trans-isomers in the azopolymer system. It serves as the mean volume fraction of these isomers. In the equation:

- c is the local concentration, or order parameter, which varies spatially and represents the distribution of cis- and trans-rich regions across the material.
- c_0 is a constant value set as the average concentration of these isomers throughout the material. It's a baseline that helps quantify the deviation of c from this average concentration, capturing local fluctuations in cis- or trans-isomer concentration,
- $B(c-c_0)$ acts as a term driving the system toward this baseline concentration c0, factoring in long-range interactions that influence the spatial patterning.

The reference concentration for cis and trans-isomers in an azopolymer system has first to consider the initial concentration of isomers in the absence of external stimuli as light. The total volume fraction of isomers in the system is ϕ_{total} and represents the combined concentration of both cis and trans isomer in the azopolymer.

Initially without illumination $\Phi_{total} = \Phi_{cis}^{eq} + \Phi_{trans}^{eq}$ is the volume fraction of trans- and cis- isomers.

The equilibrium constant $K_{cis\text{-}trans}$ gives the volume fraction of cis and trans- isomers as:

$$K_{cis-trans} = \frac{\phi_{cis}^{eq}}{\phi_{trans}^{eq}}$$

H. Galinski et al. [1] demonstrated that the formation of photoactivated patterns on azopolymer films can be fully explained through the physical concept of phase separation between two coexisting immiscible phases within the polymer. This phase separation occurs as the photoactive material transitions from a (meta)stable configuration to an unstable state upon exposure to external

perturbations, such as temperature or light. The system then evolves toward equilibrium, resulting in the emergence of two distinct immiscible phases. One phase is characterized by mass transport and molecular alignment along the polarization of the laser field, while the other undergoes spatial reorganization, leading to the development of surface relief gratings.

[1] H. Galinski, A. Ambrosio, P. Maddalena, F. Capasso, PNAS, 111, (48), 17017-17022, (2014).

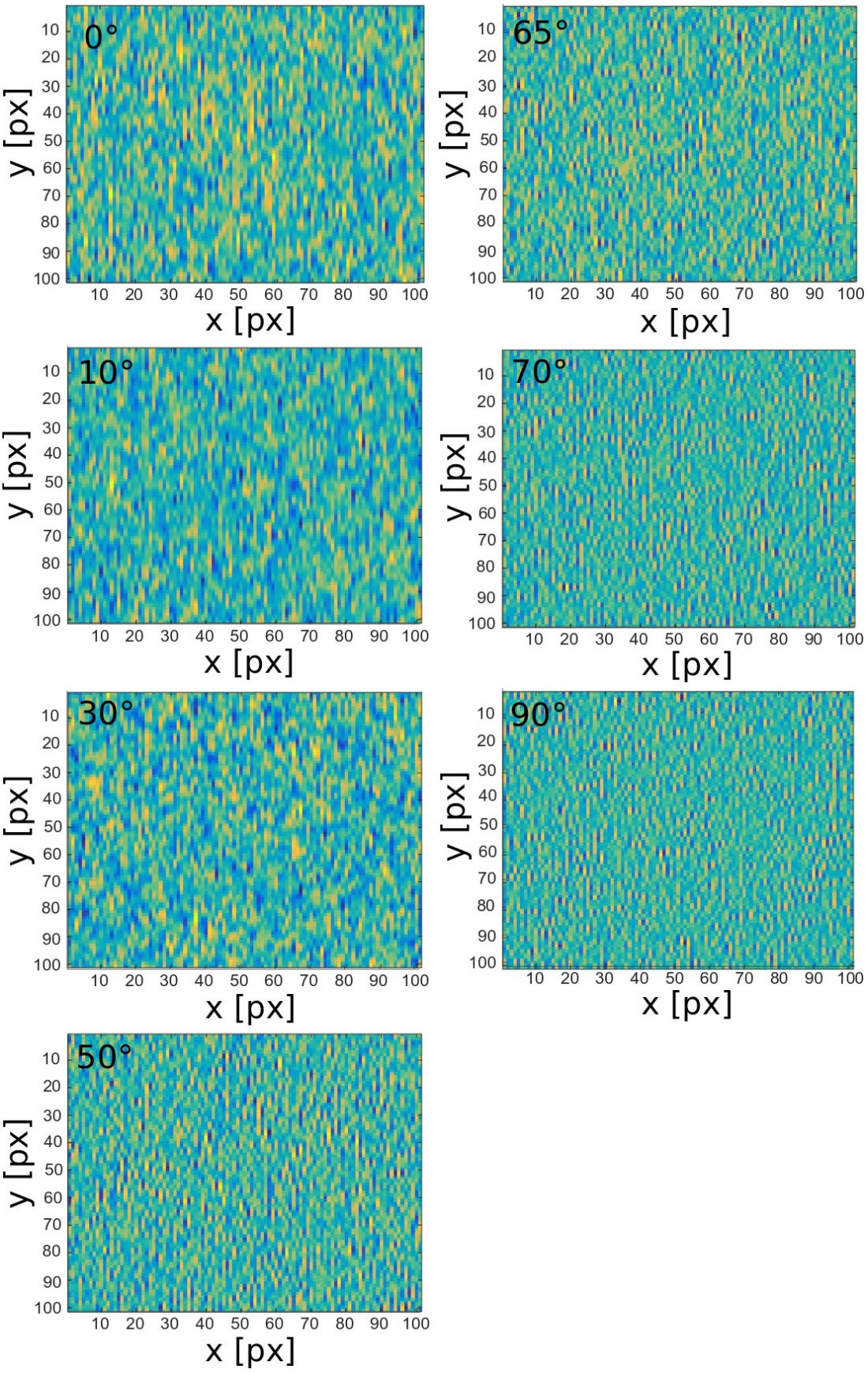

Fig. SI4: Simulation of the illuminated patterns when the laser with a fixed polarization and a laser with a changed polarization simultaneously illuminate a thin azopolymer film.

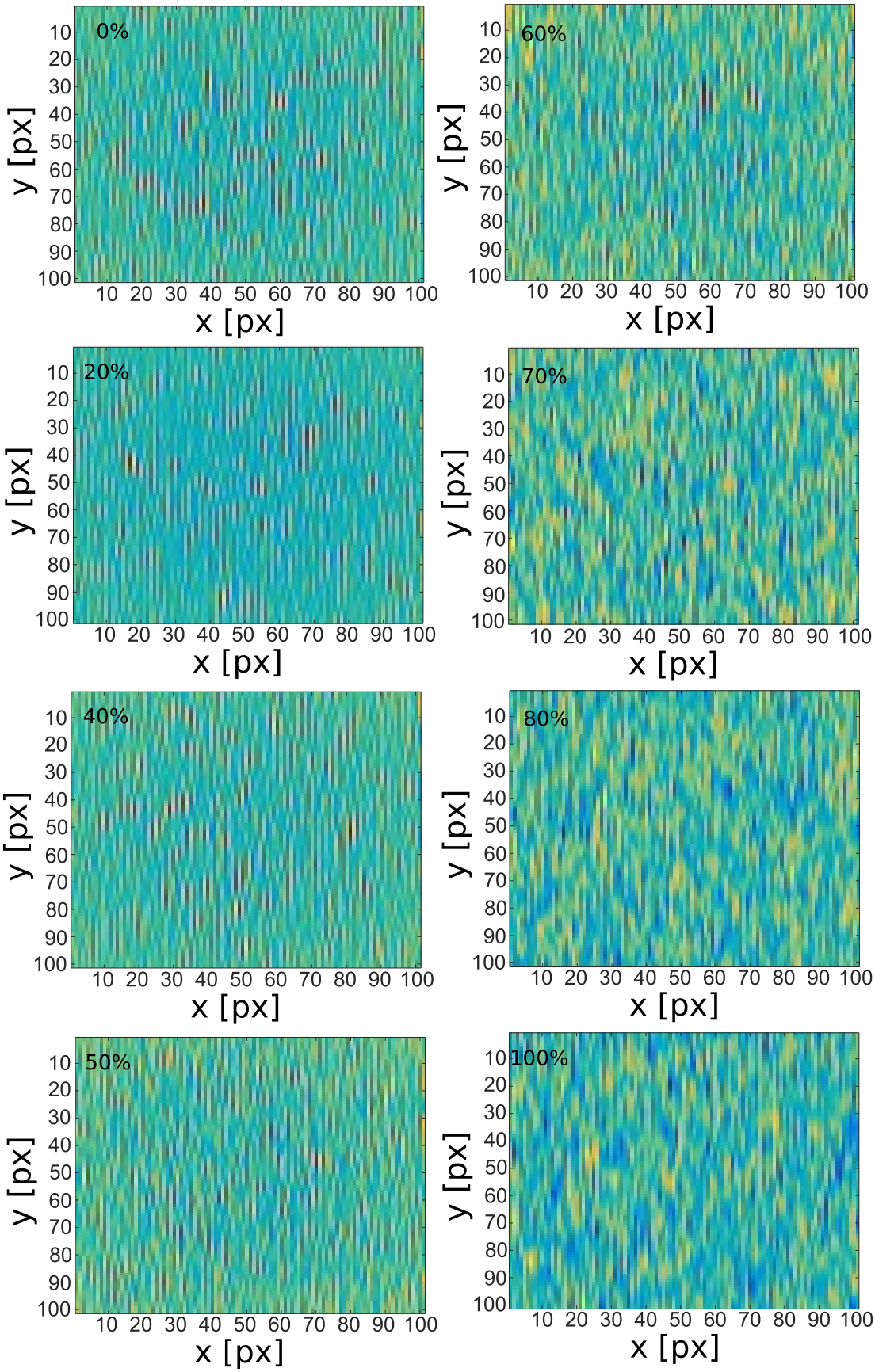

Fig. SI5: Simulation of the illuminated patterns when the laser with a fixed polarization and a laser with a spatial changed coherence simultaneously illuminate a thin azopolymer film.