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Super-twist generation and instabilities in photosensitive liquid crystal cells

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ABSTRACT

In planar nematic liquid crystals cells twist deformation was generated through photoalignment. By increasing the twist angle gradually, supertwisted cells were constructed in the range of 2π–3π twist angle. The supertwist relaxed through the formation of either π or 2π inversion loops, depending on the character of the photosensitive substrate. The difference in the relaxation process can be related to the zenithal anchoring strength on the photosensitive plate.

1. Introduction

The phenomenon of photoalignment, i.e., the light-induced change of liquid crystal orientation on surfaces, was discovered in the early 1990-s by Yuriy Reznikov's group [1] and W. Gibbons [2,3]. For reversible photoalignment most often *trans-cis* isomerization of azo dyes [4] is exploited to control the surface director orientation by a polarized light beam. The azo dyes are either coated on the substrate as a molecular layer or embedded in a polymer film. When polarized irradiation is applied, light-induced conformational transitions from the *trans* to the *cis* state and back-relaxation to the *trans* conformer induces an orientational order of the azo-dyes. The order is transferred to the liquid crystal in contact with the photosensitive layer. With most azo-dyes the liquid crystal is aligned parallel to the substrate and perpendicularly to the light polarization.

In a typical experiment a liquid-crystal sandwich cell is constructed with one photosensitive substrate and one traditionally prepared "reference" plate, which ensures fixed planar orientation (e.g., a plate coated with polyimide and rubbed unidirectionally). Regarding the light irradiation, it can be either "direct", i.e., the light enters the cell through the photosensitive plate, or "reverse" when the light input is from the reference side [5].

Photoalignment provides the possibility to create twisted nematic liquid crystal layers, in which the director rotates from the reference substrate to the photosensitive one by an angle of Φ. Starting from a planar cell, it is straightforward to induce a twist angle in the range $-\pi/2 < \Phi < \pi/2$; the photosensitive plate should be irradiated with a light beam polarized by an angle between 0 and π with respect to the director alignment on the reference plate. Twist angles outside the range $-\pi/2 < \Phi < \pi/2$ can be also induced if the polarization direction is gradually increased, "winding" the nematic layer over the limit of $\pi/2$. The minima of the twist energy (Φ_m) always corresponds to a total rotation of the director across the cell between $-\pi/2$ and $\pi/2$, but the transition of the director configuration from $|\Phi| > \pi/2$ to the appropriate Φ_m cannot occur in a continuous way. In this manner metastable "supertwisted" structures can be created. The supertwist eventually relaxes back to the stable twist configuration through the formation of inversion walls.

The main subject of the present paper is the investigation of the light-induced supertwisted structures and in particular their relaxation process back to the stable twisted configuration. We compared two kinds of photosensitive substrates. In the first type a monolayer of an azo-dye was attached chemically to a glass plate. In the second type of photosensitive plate, the azo dye was incorporated in a polymer host as a side-chain. We found that in both types of cells the orientation followed almost exactly the direction perpendicular to the light polarization. However, the relaxation of the supertwist occurred through different types of inversion walls in the two cases, which indicates different mechanisms of relaxation. An essential difference was noticed also using the reverse geometry: in the case of azo monolayer light-induced instabilities were observed [5,6,7], which were not found in the case of the azo-functionalized polymer. In the paper we suggest that the difference in zenithal anchoring strength is responsible for

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the diverse behaviour observed in the presence of the two kinds of photoaligning layers.

2. Experimental details

2.1. Sample preparation

Two types of photosensitive plate were prepared. In the first one a silane derivative of the azo compound methyl-red was used (dMR, see Fig. 1a). The dye was chemically attached to a clean glass substrate and formed a monolayer [8]. For the second type, the polymer polymethyl-methacrilate was functionalized with the azo-dye Disperse Red 1 (pDR1, see Fig. 1b). The functionalized polymer was dissolved in toluene and spin-coated on the substrate. The basic photoorientation process for the two materials were described in [8,9], respectively.

The reference plates were rubbed polyimide coated slides from E.H. C. Co (Japan). The sample thickness were in the range 20–30 μm and were filled either with 4-cyano-4′-penthylbiphenyl (5CB) or with mixture E7 from Merck. Before filling the material, the cell was illuminated with white light, polarized perpendicularly to the rubbing direction. This procedure ensured a good quality planar initial alignment of the nematic liquid crystal.

2.2. Experimental setup

For qualitative observations a beam from a diode laser (wavelength 409 nm) was coupled into a polarizing microscope and irradiated the sample with fixed polarization. The stage was rotated slowly by hand while the sample was viewed in the microscope. For quantitative measurements the setup sketched in Fig. 2 was used. A beam from a DPSS laser (wavelength 457 nm) was converted to circular polarization and let through a slowly rotating polarizer (Fig. 2a). The light entered the cell from the photosensitive side (direct geometry). It was defocussed to a spot size around few mm. The rotation speed of the polarizer was chosen slow enough that the twist deformation in the cell could follow adiabatically the surface reorientation.

In order to detect the orientation on the photosensitive plate a polarized probe beam from a He—Ne laser (wavelength 633 nm) was sent through the cell, entering it at the reference plate (see Fig. 2b). The probe beam was positioned to the center of the pump beam. Behind the cell the probe beam crossed a polarizer (FRP), which was rotating with a frequency around 60–70 Hz. The intensity of the beam behind the polarizer was measured by the photodiode PHD, connected to a lock-in-amplifier (LA). In order to generate a reference signal for the lock-in amplifier, another signal, polarized in the same direction as the probe beam, was also sent through the FRP and its intensity was measured by the photodiode R_PHD. The lock-in amplifier provided the phase, θ, and the amplitude of the probe-beam signal A (Fig. 3).

In the Maguin limit of light propagation [10] $\Phi = \theta/2 + n\pi$ ($\theta = 0$ corresponds to a planar cell, n is an integer). The depolarization ratio, defined as $D = 1 - A/A_0$, where A_0 is the amplitude for the planar cell, indicates the deviation from the Maguin limit and can be used – in principle – to deduct the number of full turns of the director, n. Model calculations, based on de Vries theory [10] showed, however, that the depolarization ratio for a monochromatic light becomes an oscillating function of Φ for twist angles larger than about 2π. The depolarization is very sensitive to the sample thickness; changes of less than a micrometer can shift the maxima of the D vs. Φ curve considerably. This circumstance renders quite difficult to fit the measured curves to the theoretical ones. On the other hand, sharp changes in the detected depolarization ratio can be considered as a sign of a jump in the number of turns of the twisted structure. In the experiments we exploited this fact.

3. Results

In Fig. 4 an experimental result is shown with the dMR coated sample, filled with the liquid crystal E7. In the experiments the starting pump polarization was perpendicular to the director.

During the measurement the polarization direction of the irradiating light completed 5 full 360° turns; the rotation speed was 2°/s. If it is assumed that there are no discontinuities in the twist angle, one would find that $\Phi_{app} \approx \alpha$ during the whole period of rotation. Here α is the rotation angle of the polarizer, ranging from 0 to 1800° (see Fig. 4a). However, we observed sharp decreases in the depolarization ratio at certain times. These decreases occurred periodically; in the case of dMR it took place approximately at $\alpha \approx m \times 360^{\circ}$, with $m = 1, 2, 3\ldots$ We attribute the observed drops of the depolarization to the formation and expansion of inversion walls, which reduce the twist angle by 360° (Fig. 4b). The periodic change of the depolarization ratio is superimposed on a continuously increasing background. The background is probably due to the permanent formation of defects in the sample, which contribute to scattering and depolarization of the probe beam. We associate the reduction of the twist angle with the maxima of the depolarization ratio, in a somewhat arbitrary manner. The periodic repetition of the D curve, however, shows clearly the periodic reduction of the twist angle.

The result obtained for a sample with pDR1 layers is depicted in Fig. 5. As in the previous case, the „apparent" twist angle followed the rotation angle of the pump beam polarization. We observed similar periodic drops of the depolarization ratio. The first drop occured at $\alpha \approx 465^{\circ}$, a somewhat higher value than for dMR. The successive drops followed each other at every 180° rotation of the polarization, indicating the formation of π walls, in contrast with the 2π walls, observed with dMR layers. The minimal values of the depolarization ratio is 0.2, which indicates that the twist was reduced with a value of near 180°. The increase of the background value of D is much less pronounced than is the case of dMR.

An essential difference was found in the behaviour of the two types of cells after ending the irradiation. In the case of dMR-coated cell, the inversion walls moved to the edge of the laser spot, where they became stable for several months. The disclination loops surrounding the irradiated area were visible to the naked eye, due to scattering. On the other hand, in the pDR1 cells the inversion loops disappeared in few minutes after the irradiation finished. As revealed from observations in the

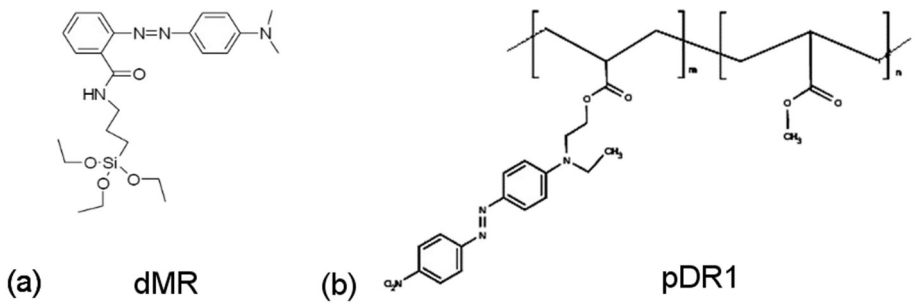

Fig. 1. (a) Structure of dMR (b) Structure of the azo-functionalized polymer, pDR1.

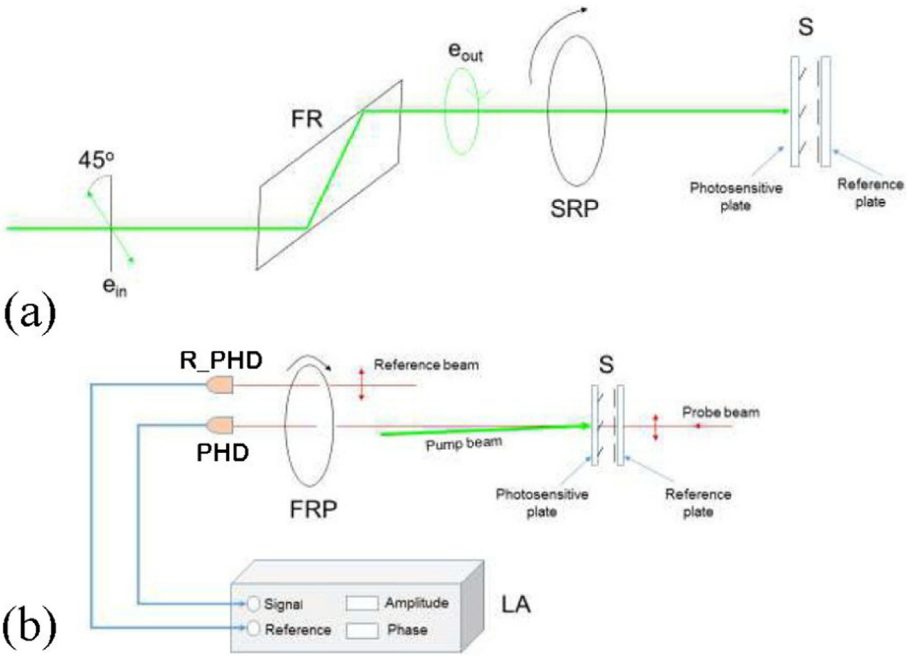

Fig. 2. Experimental setup. (a) Pump beam. FR: Fresnel rhomb. SRP: Slowly rotating polarizer. S: sample. (b) Detection of the orientation on the photosensitive plate. FRP: fast rotating polarizer. LA: lock-in-amplifier. S: sample. PHD: photodetector for the probe beam. R_PHD: photodetector for the reference beam.

polarizing microscope, first a split occurred in the loop, then the free ends were propagating along the loop until it disappeared completely. The initial planar configuration was restored, without any sign of the inversion loops. This fact may also explain that the background of the depolarization ratio is almost constant during the successive rotations of the polarization of the pump beam (Fig. 5) in contrast to the case of dMR (Fig. 4).

The qualitative observations in polarizing microscope for the direct geometry were in accordance with the measurements. However, because using the coarse method of rotating the microscope stage by hand, the inversion loops were less regular. In addition, we investigated in the polarizing microscope the reverse geometry, i.e., irradiating the sample beam from the reference plate. We showed in previous publications that for dMR cells in this geometry dynamic instabilities occur in the cell. In the case of laser irradiation the presence of instability was deduced from light scattering. Now we observed it directly under the microscope and confirmed that the instability was caused by the formation, propagation and annihilation of disclination loops, as suggested in [6]. On the other hand, in the case of pDR1-coated photosensitive plates, no instabilities took place. Switching on the laser beam, the texture of the nematic film in the initial few tens of seconds showed some transient changes; subsequently it became stable. (See Fig. 6a and b and the corresponding video links.)

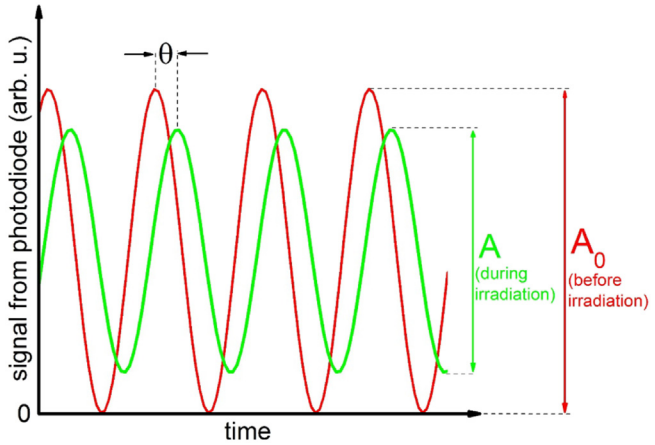

Fig. 3. The signal from the photodiode before and during the irradiation.

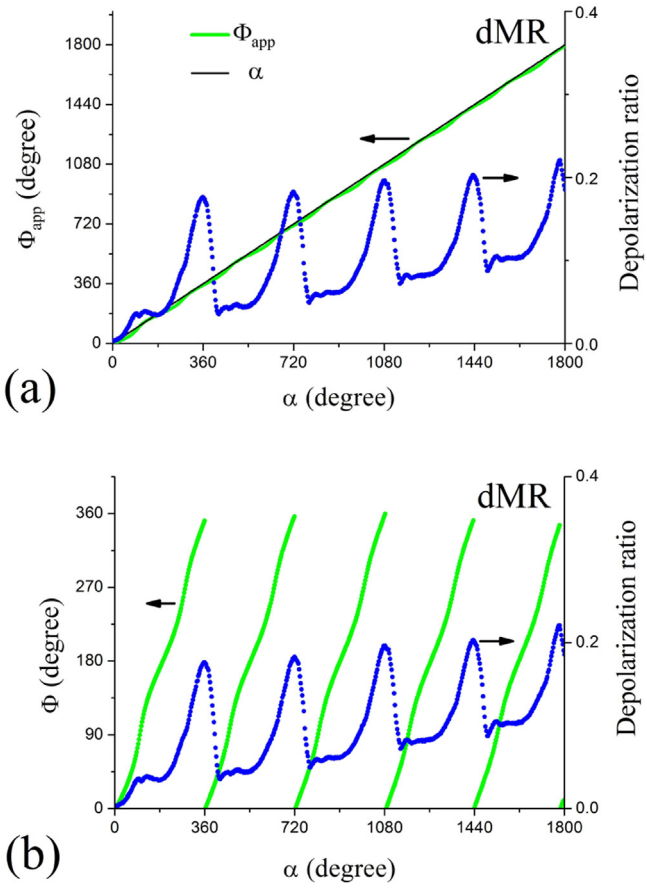

Fig. 4. The „apparent" (a) and the (b) actual twist angle and the depolarization ratio as a function of the angle of polarization of the pump beam for dMR.

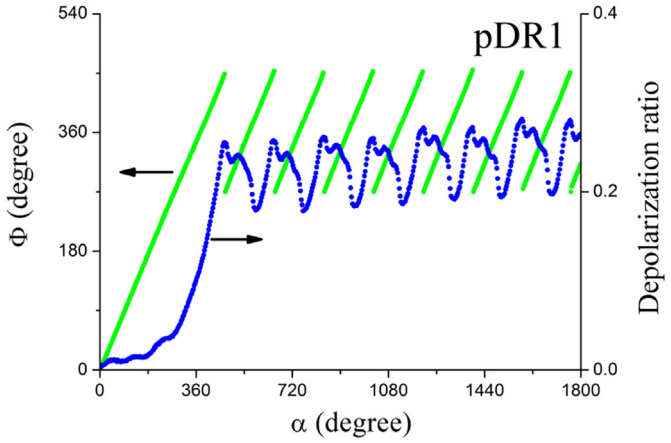

Fig. 5. The actual twist angle and the depolarization ratio as a function of the angle of polarization of the pump beam for pDR1.

4. Discussion

In the experiments with both types of cells, no significant deviation between the normal to the polarization direction of the reorienting light and the director orientation on the photosensitive plate was found, even in the case of supertwists over 360°. This fact indicates strong photo-induced anchoring. (1° of deviation at 360° twist in a 20 μm thick cell corresponds to an azimuthal extrapolation length of 55 nm.)

We found that with the dMR based photosensitive system a relaxation process occurred when the twist angle was increased above 2π. The reduction of the twist angle took place through the formation of an inversion wall of 2π, decreasing the twist angle to around 0. Following this reduction, the twist angle increased again until 2π, when it was yet again reduced to 0 via an inversion loop and so on. In the polymer system inversion walls were formed once more when the twist angle was above 2π. The relaxation took place, however, through inversion walls of π, reducing the twist angle from 2π to π. Inversion loops appeared therefore after every π rotation of the polarization of the irradiating light. A further difference between the two kinds of photosensitive layer was that in the first case after stopping the irradiation a permanent inversion wall remained at the edge of the light spot. On the contrary, in the pDR1 based system after the irradiation ended the inversion walls disappeared and the uniform director orientation was restored in a few minutes.

We discuss in the followings which factors determine the stability of the supertwist, and by what mechanism are the inversion walls formed. It is obvious from the experiments that the mechanism is not the same for the dMR and the pDR1 coated substrates. As the liquid crystal material and the reference plate were the same in both cases, furthermore the azimuthal anchoring was in both cases strong, we suggest that the difference originates in the strength of zenithal anchoring of the liquid crystal molecules on the photosensitive substrates.

First we examine the case of strong (infinite) zenithal anchoring. It can be shown from the continuum theory of nematic liquid crystals [11], that if the relation $K_3 > 2K_2$ holds, at strong anchoring conditions the planar twisted structure is stable against small out-of-plane bulk director fluctuations for arbitrary large twist angles (K_3 and K_2 are the bend and twist elastic constant respectively.) This relation holds for most of the nematic liquid crystals, including 5CB and E7, which were used in the present study. When that is the situation, there is no possibility to reduce the twist angle in a continuous way; instead the nucleation of an inversion wall takes place. The wall expands, and in its inside region the twist is restored to its minimal value.

When the zenithal anchoring energy is finite (weak anchoring), there exists a surface torque in the boundary layer, which attempts to rotate the liquid crystal molecules adsorbed to the substrates. In a perfect planar twisted cell for symmetry reasons the surface torque does not have a component, which would create zenithal tilt at the boundaries. Nonetheless, it is evident that at a very high supertwist the total free energy of the system decreases if at least on one of the surfaces the orientation becomes homeotropic, as the increase of surface energy is compensated by the reduction of the large elastic twist energy. Therefore, a critical twist should exist at which the planar orientation becomes unstable, even if the inequality $K_3 > 2K_2$ is satisfied. The critical twist is proportional obviously to the zenithal anchoring strength. We plan to discuss quantitatively this transition in a forthcoming publication.

We suggest that in the case of the dMR layer the zenithal anchoring is strong, therefore zenithal transition of the nematic layer did not take place; the inversion wall was formed through nucleation, as described above. In this case, the inversion wall is attached to the surface and does not relax after the irradiation is finished.

On the other hand, we propose that in the case of pDR1 the zenithal anchoring strength is finite and the observed maximum supertwist is higher than the critical twist for the out-of-plane transition of the nematic layer. As a consequence, zenithal tilt of the director takes place at the polymer surface during the generation of the supertwist. High enough zenithal tilt allows to unwind the twisted layer. However, while unwinding is occurring the twist angle decreases below the critical value and the planar orientation is restored; in this way the unwinding process ends. This circumstance could explain why the twist angle is reduced in the case of pDR1 only by π.

The suggested transition on pDR1-coated plates may take place locally because inhomogeneities in the photosensitive layer may occur. In this case a small inversion loop is formed in the sample, and it expands similarly to the case of dMR layer. However, this inversion wall does not have core and it is not attached to the surface.

We assume that the weak zenithal anchoring on the pDR1 surface is induced by the irradiation. The *trans-cis* isomerization redistributes the dye molecules, so that their long axis will lay preferably in a plane

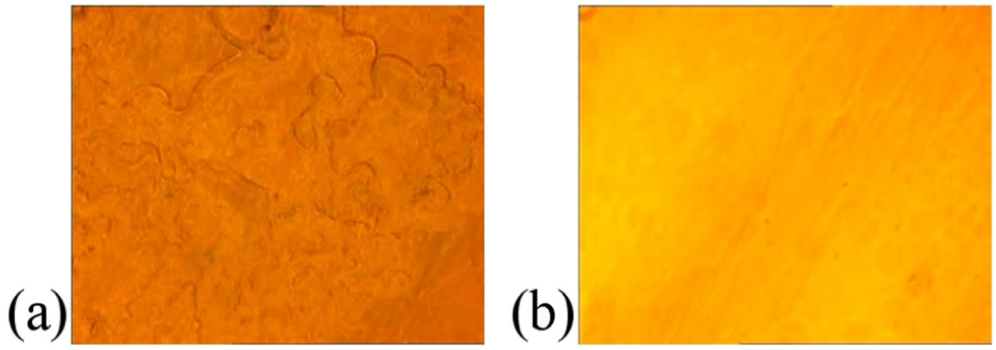

Fig. 6. Microscopic images of dMR (a) and pDR1 (b) samples, taken in the reverse geometry under illumination with 409 *nm* laser diode having a polarization at α ≈ 45°. The corresponding movies can be found in the Supplementary Material (dmr_rg.mp4 and pdr1_rg.mp4 for the dMR and pDR1 sample, respectively).

perpendicular to the light polarization. This plane contains also the sample normal, hence a part of the dye molecules is oriented perpendicularly to the plane of the photosensitive layer, weakening the zenithal anchoring strength. With dMR no such possibility exists since the molecules are chemisorbed to the glass plate in a monolayer.

The same mechanism can account for the lack of laser-induced instabilities in the reverse geometry for pDR1-coated plates. As discussed in detail in [6,7] for the case of dMR, laser irradiation generates instabilities in the sample by spontaneously winding up the nematic. It was shown, however, that when the phase difference of the extraordinary and ordinary rays of the irradiating beam across the nematic layer is $(n + 1/4)\pi$ (n integer), no instabilities occur. For $\alpha = 45^{\circ}$ incident polarization this condition means that the incidentally linearly polarized beam becomes circularly polarized at the photosensitive plate. If the zenithal orientation at the surface changes with increasing twist (as we suggest for pDR1 films), the phase difference between the two components also changes. Eventually the above condition should be fulfilled, therefore a stationary twist is stabilized instead of an unstable configuration.

The stability limit of the supertwist remains an open question. The experiments show that this limit for pDR1 is somewhat higher than for dMR. A possible explanation of this fact could be that in the case of the former system the onset of the zenithal tilt occurs already at smaller twist angles than the stability limit for the formation of a 2π inversion wall in planar cells. This circumstance can change the mechanism of the onset of inversion wall, as explained above.

Experiments are currently in progress to demonstrate in a direct way the light-induced zenithal tilt of the nematic director at the pDR1-coated plates.

5. Conclusions

We showed that with the help of slow rotation of the polarization direction of a pump beam, supertwist can be generated in an initially planar nematic cell. Supertwists over 2π could be created. We found two distinct mechanisms of the instability of supertwist. The first one is effective for a monolayer of azo-dyes, the other for an azo-functionalized polymer layer. It is assumed that the difference between the two cases rests in the zenithal anchoring on the corresponding photosensitive plates. In particular, the former system exhibits strong zenithal anchoring, while in the later one it is weak. With this assumption one can also explain the absence of light-induced instability in the polymer coated photosensitive plate.

The procedure described in this paper gives the possibility to generate inversion walls in addition to methods applied earlier, such as the use of magnetic fields [12–14] or bulk optical reorientation [15]. We proposed an explanation for the development of the π walls. However, the interesting question arises that how the 2π walls – exhibiting a singular core – are formed. There are models to describe the formation of singular defects formed during the isotropic-nematic phase transition [16,17], but to our knowledge there is no theoretical description of a similar process within the nematic phase. Monte-Carlo simulation might be helpful to elucidate this problem.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2017.12.071.

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