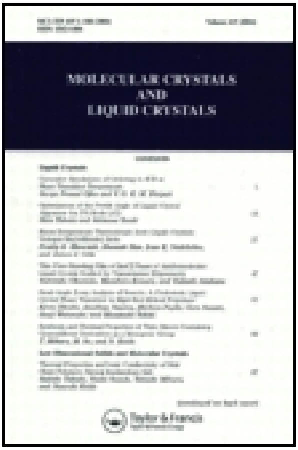

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LC Alignment Controlled by Photoordering and Photorefraction in a Command Substrate

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LC ALIGNMENT CONTROLLED BY PHOTOORDERING AND PHOTOREFRACTION IN A COMMAND SUBSTRATE

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As command substrates in liquid crystal (LC) panels, azopolymer films have been widely studied over past decade. These studies were mainly caused by photoordering and photorefraction effects allowing to control LC alignment. Earlier, the mentioned effects were used separately. In the present study, a layer of azopolymer acts both as photoaligning and photorefractive substrate. The photoordering effect is used to align LCs homogeneously, whereas effect of the specific photorefraction is employed to modify boundary conditions. The latter ones were spatially modulated by the sample exposure to interference patterns formed by two coherent laser beams. Multiple orders of diffraction are observed in samples tilted with respect to the beam incidence bisector when the samples are biased by a dc external electric field with the intensity close to the Frederiks threshold. Possible grating recording mechanisms are discussed.

Keywords: azopolymer; liquid crystal; photoalignment; photoconductivity; photorefraction

1. INTRODUCTION

Azopolymers are the polymers containing aromatic azo groups (usually substituted azobenzenes) incorporated in the main or side polymer chains. These compounds attract great attention over past decade because of several outstanding properties. One of them is a highly efficient photoordering

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*Corresponding author. E-mail: olegyar@iop.kiev.ua, matczyszyn@kchf.ch.pcor.wroc.pl caused by strong absorption dichroism of azobenzene units [1–5]. This feature makes azopolymers promising for a number of photonic applications concerned with information processing and storage, information displays and telecommunications.

One more distinctive feature of azopolymers is its ability to align liquid crystals. At first, Ichimura *et al.* [6] showed that azo compounds can be used to switch LC from homeotropic to planarly oriented state. Later on, Gibbons *et al.* [7] realized in-plane reorientation of LC using azopolymer as a command substrate. In this experiments the ability of azochromophores to undergo E/Z isomerization and to reorient perpendicularly to the direction of light polarization has been employed.

The other possibility to control LC alignment in the cells containing azopolymer substrate is based on the effect described in [8–10] and named as non-classical photorefraction. In these experiments LC cells were used in which a primary homegeneous LC alignment is achieved by unidirectional rubbing of the azopolymer substrate. The two-wave mixing in these cells leads to highly efficient diffraction gratings, when two conditions are satisfied:

1. the cells is biased by a dc external electric field with the intensity close to the Frederiks threshold.
2. the cell is tilted with respect to the beam incidence bisector.

It is assumed that the writing beams work on the photoconductive azopolymer substrates causing spatial charge modulation and, possibly, grating formation, if electro-optic effect takes place. This last term means that the refractive index of the material will depend on the intensity of the electric field generated by the separated charges. The described mechanism corresponds to classical photorefraction. The secondary grating, experimentally detected, is formed in LC layer under influence of the command substrate. On the one hand, the grating in LC layer is governed by command substrate. On the other hand, the parameters of LC grating can be independently controlled by the sample inclination and the intensity of the external electric field. Same as in case of classical photorefraction, light intensity redistribution between pumping beams was observed. At the same time, the revealed phenomenon was not identical to classical photorefraction.

The idea of the present study is to combine photoalignment and specific photorefraction methods of LC alignment control by the use of dual function azopolymer substrates. The photoalignment ability of the substrates is used to obtain primary homogeneous alignment of LC layer, whereas the photorefraction is employed for spatial modulation of the primary alignment. The advantages of this approach as well as the grating recording mechanisms are discussed.

2. EXPERIMENTAL DETAILS

2.1. Sample Preparation

As LC photoaligning substrates, the films of polyamic acid solution of Disperse Orange 3 (4-(4-nitrophenylazo)aniline, Aldrich Chemicals) were used. The excellent LC aligning properties of this material were discovered earlier in [11]. The layers of this composition were spin coated on the quartz or ITO covered glass slabs and subsequently heated for 2 h at 220°C. The backing causes imidization of polyamic acid and, possibly, covalent attaching of azo dye to polymer backbone through amino group. This may result in some bleaching of the active layer. The UV/Vis absorption spectra before and after baking are presented in Figure 1 (Curves 1 and 2, respectively).

The film thickness measured with profilometer was 100–200 nm. To generate anisotropy, the films were illuminated for 30 min with UV light from the mercury lamp polarized by Glan-Tompson prism. The light intensity in the sample position was about 5 mW/cm^2.

The UV/Vis spectra of the polymeric film after illumination depend on the testing light polarization. The maximal value of absorption, $D_\perp$, is detected for the testing light having polarization E_t perpendicular to the direction of the exciting light polarization E_{ex}, whereas minimal absorption,

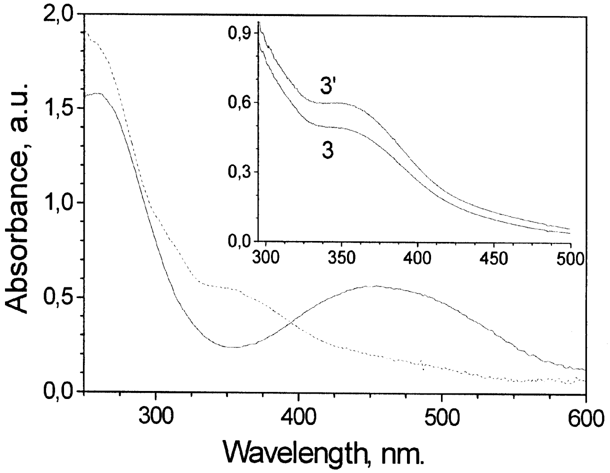

FIGURE 1 UV/Vis absorption spectra of azopolymer before backing (curve 1), after backing at 220° over 2 h (curve 2) and after illumination with polarized light (curves 3 and 3'). Curves 3 and 3' denote polarized spectra measured for $E_t \| E_{ex}$ and $E_t \perp E_{ex}$, respectively.

$D_{\|}$, was detected for $\mathbf{E_t} \| \mathbf{E_{ex}}$ (respectively, curves 3′ and 3 in Figure 1). It shows alignment of azo dye fragments in the direction perpendicular to $\mathbf{E_{ex}}$. The mechanisms of photo-orientation in azopolymers are considered minutely in [2,5].

The cells were assembled from two ITO covered glass slabs containing spin coated photo-oriented polymer layers. The slabs were sandwiched in parallel to each other. The cell gap was maintained with the spacer of a 12 μm. Two types of liquid crystal mixtures were used to fill-up the panels: the mixture of cyanobiphenyls E7 (Merck) – in panel Pl and ZLI 4801-000 (Merck) – in panel P2.

2.2. Methods and Experimental Set Up

The UV/Vis spectra of azopolymer films were measured by KSVU spectrometer (LOMO, Russia). A quality of LC alignment in the prepared cells was controlled by observation in polarizing microscope. Pretilt angle of LC alignment was measured by crystal rotation method [12].

A classical degenerate two wave mixing system was used for grating recording. The scheme of the system is shown in the Figure 2. Two beams of the He-Ne laser from Spectra Physics ($P = 25\,\text{mW}$, $\lambda = 632.8\,\text{nm}$) crossed at the angle 2θ and incident onto a cell tilted at the angle α. The beam diameters were 1.5 mm giving effective light intensities (about $400\,\text{mW/cm}^2$ for each of them) within a sample. Direction of light polarisation was parallel to the planar alignment of liquid crystal panel. The external

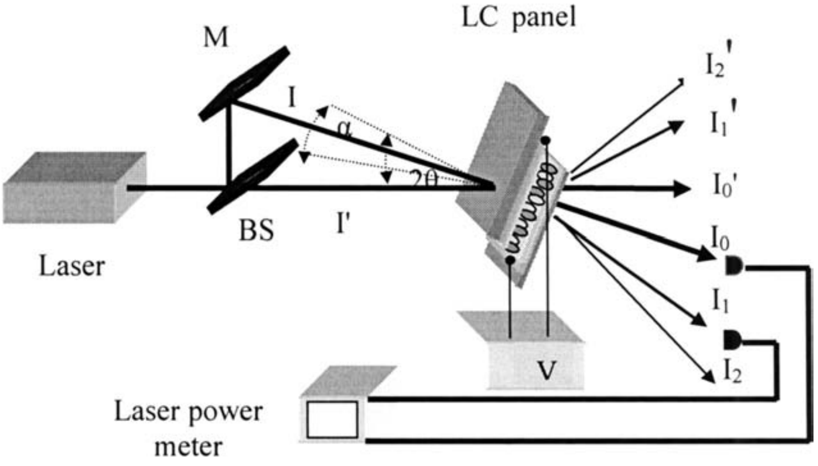

FIGURE 2 Schematic representation of the two-wave mixing experiment. BS-beam splitter, M-mirror, V-dc voltage supplier.

voltage U was applied to the sample to cause suitable arrangement of liquid crystal molecules.

The measurements were performed for different conditions -2θ equal to: 2.4°, 2.8°, 3.4°, 4.6°, 7°, subsequently, and α from the range of 0° to 60°. The convergence angle 2θ was varied to control the period of interference fringes and, hence, grating period, according to the relation $\Lambda = \lambda/2\mathrm{n}\sin\theta$. The tilt angle α has been used to vary sensitivity of the method to LC director modulation. The dependencies of diffraction efficiency η versus U, 2θ, α, and dynamics of the gratings recording were checked with a use of the two-head laser power meter Labmaster Ultima, Coherent. Both types of samples, P1 and P2, were measured in the same experimental conditions, and results were compared.

3. RESULTS

High quality planar LC alignment was observed in the cells filled with both types of LCs. Making combined cells, consisted of rubbed polyimide substrate and photoirradiated azopolymer substrate, we revealed that LCs are aligned in the direction of azo dye photo-orientation, i.e., perpendicularly to E_{ex}. The LC pretilt angle estimated by crystal rotation method was close to 0.

In two-wave mixing experiments, multiple order of diffraction were observed. The experimental grating characteristics obtained for P1 and P2 samples were fairly similar except the cases described below. The results of measurements of the diffraction efficiency $\eta = I_1/I_0$ (I_1 and I_0 are laser beam power diffracted into first-order and a power of zero-beam, respectively) as a function of voltage applied to the sample, are shown in Figure 3. For low voltages, the diffraction efficiency is equal to 0 and it increases with the increase of the applied voltage. Maximum of diffraction efficiency is observed for external voltage $U = 9\,V$. In the following, the $\eta(U)$ curve decreases.

Figure 4 shows the dependence of the diffraction efficiency versus light intensity. The $\eta(I_0)$ function is quasi-linear in a wide intensity range. It shows that these samples can effectively act in a wide range of light intensities without destruction and saturation effects.

The $\eta(\alpha)$ curve is presented in Figure 5. For non-tilt conformation, when the input beams are directed practically parallel to the sample normal ($\alpha = 0°$) diffraction signal was not observed. When oblique incidence was realized, the diffraction orders appeared. The highest diffraction efficiency is obtained for $\alpha = 45°$.

The dependence of the diffraction efficiency η on the angle 2θ is presented in Figure 6. For smaller angles, when the grating period is bigger,

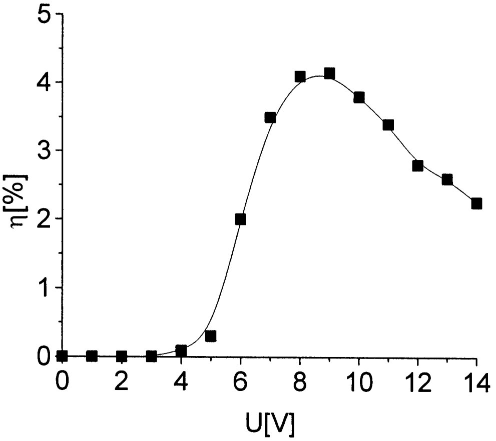

FIGURE 3 Dependence of the diffraction efficiency versus applied voltage for P1 panel. $\alpha = 45°$, $2\theta = 2.8°$.

higher diffraction efficiency is achieved. In the Figure 6 there are also presented values of external voltage U, which were applied to obtain maximum of the diffraction efficiency. The values of U are presented for different periods of grating. The smaller is 2θ angle, the lower U is needed to reach maximum of η. The value of η asymptotically grows when the angle 2θ decreases. Because of it, the best condition to achieve high diffraction efficiency is to build system with a large period of holographic grating.

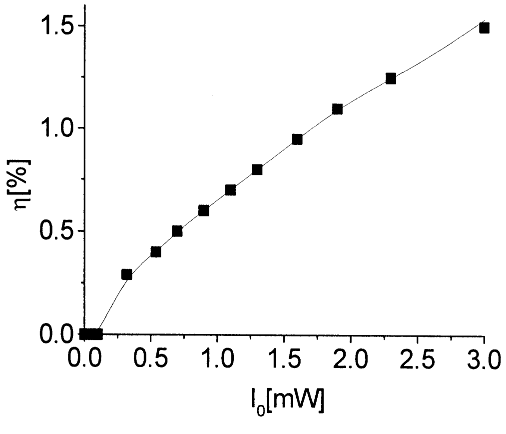

FIGURE 4 Dependence of the diffraction efficiency on light intensity for panel P1. $\alpha = 45°$, $2\theta = 2.8°$, U = 9.5 V.

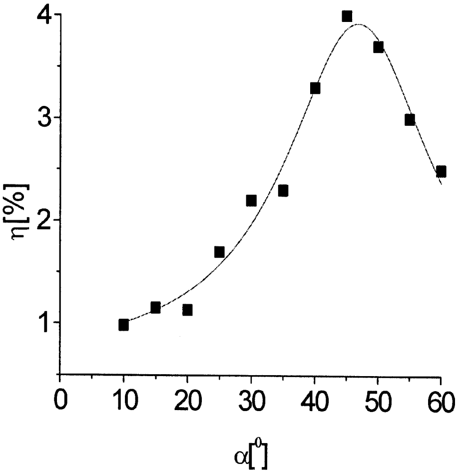

FIGURE 5 Dependence of the diffraction efficiency vs. tilt angle α for P1 panel. $2\theta = 2.8°$, $U = 9.5\,V$.

The dynamics of the grating recording depends on the nature of the liquid crystal used in the panel. This process in the sample P1 filled with E7 is relatively slow (about several minutes). The recording curve for

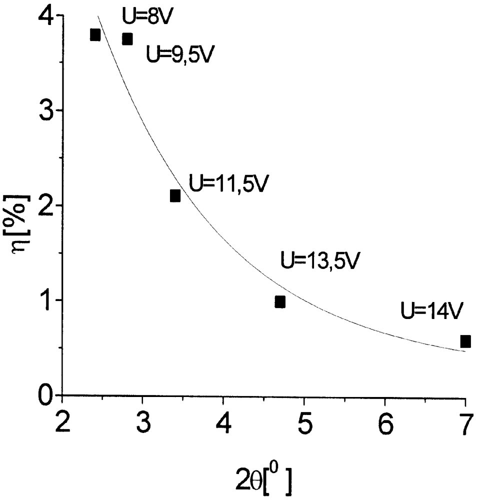

FIGURE 6 Dependence of the diffraction efficiency on an angle 2θ for P1 panel. $\alpha = 45°$, $U = 9.5\,V$.

the panel P2 (filled with LC ZLI 4801) is presented in Figure 7. Evidently, the recording time is about 1 min. The additional measurements showed that the time depends strongly on the intensity of recording beams, grating period, and applied voltage.

Some grating characteristics for our cells are determinative for classical photorefraction. For instance, substantial redistribution of light intensity between two zero orders was observed at the value of applied voltage close to the Frederiks threshold.

Finally, let us evaluate some parameters of the induced gratings. The maximal value of η, achieved at $2\theta = 2.4^\circ$, is 4%. Taking into account expression for phase retardation $\Phi = \pi\Delta n^{eff}L/(\cos(\theta)\lambda)$ (L- thickness of the panel and λ-wavelength of the incoming light) [13] one can obtain that effective refractive index (Δn^{eff}) corresponding to $\eta = 4\%$ is equal to 0.007. This modulation is one of the highest known modulations of refractive index for photorefractive materials [14].

Approximating curve $\eta(\theta)$ one can see that grating should be detectable even for $2\theta = 10^\circ$ ($\eta \approx 0.1\%$). Using formula $\Lambda = \lambda/2n\sin\theta$ one can obtain that value $2\theta = 10^\circ$ corresponds to $\Lambda \approx 1\,\mu m$. This means that spatial resolution of our samples is better then 1000 lines per millimetre. Hence, studied system is effective non-linear medium with a great potential for a number of holographic applications.

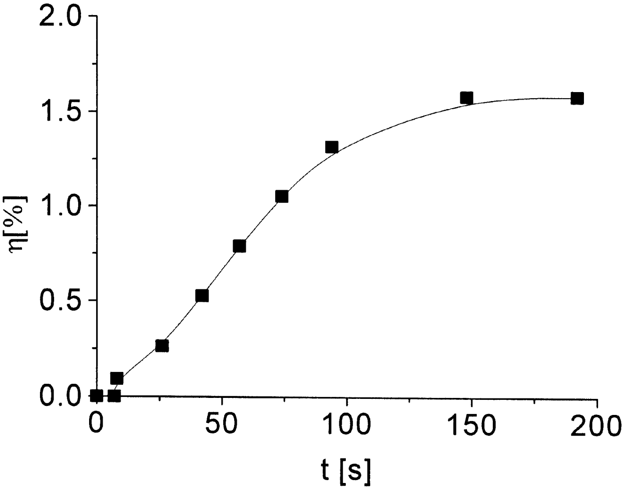

FIGURE 7 Dynamics of the holograms writing for panel P2. $\alpha = 45^\circ$, $2\theta = 2.8^\circ$, $U = 9.5\,V$.

4. DISCUSSION

In this paragraph we would like to discuss possible grating recording mechanisms. Since our system is complex, several mechanisms associated with LC and polymer substrates should be considered. First of all, we should point out possible orientational non-linearity of LC layers caused by photoinduced reorientation of LC director in the electric field of light [15]. Indeed, similarly to our results, the mentioned kind of non-linearity realises at the oblique incidence of the recording beams with the efficiency strongly dependent on the incidence angle. However, this mechanism cannot be responsible for grating recording in our studies, because of several reasons. Firstly, orientational non-linearity of non-dyed LCs realises at the intensities much higher then the intensity of recording beams used in our experiments. Secondly, in contrast to our results, the orientational gratings can be recorded even without external electric field. The low intensity orientational non-linearity, typical for dyed LCs [16,17], cannot be realised too, since azo dye containing polyimide is insoluble in LC. This fact was additionally proven by extracting LC from the cell and comparison of its UV/Vis spectrum with the spectrum of pure LC. No trace of azo dye was detected. Owing to it and taking into consideration low absorption of LC at 0.63 nm (Fig. 1), one should exclude thermal as well as conformational mechanism of non-linearity associated with photo-transformation of LC molecules [18].

On account of facts discussed above we should accept that gratings are recorded either in polymer layers or in polymer-LC interface. Since azopolymers are photochromic materials, the pumping light may result in E/Z isomerisation and accompanied photoordering of azochromophores [1–5]. These mechanisms may cause grating induction in azopolymer films when recording light is spatially modulated. As a rule, the photoinduced grating in polymer bulk is accompanied with the relief grating on polymer surface [3,4]. The gratings formed by photochromic processes in polymer films may cause spatial modulation of LC alignment and so diffraction gratings in LC layers. There are weighty reasons to neglect the circumscribed mechanism. For instance, gratings formed by this mechanism should be effective at normal incidence of recording beams. Moreover, they should be observable even without electric field. This conflicts with our results.

Excluding other mechanisms one can assume that the recording mechanism is similar to that for classic photorefraction. In case of photorefraction, the spatially modulated light causes generation of electric charges and their separation, for instance, due to photoinduced diffusion [19,20]. The origin of these charges, in case of azopolymers, is not completely clear. Possibly, they are associated with photodestruction (photooxidation, chain scission etc.) accompanying E/Z isomerization of azochromophores. The result of these processes is generation of free radicals, which can serve as charge carries in our system. Due to the drift of the charge carriers from interference maximums to minimums, spatial charge distribution is shifted in phase by $\pi/2$ with respect to the light intensity pattern.

The spatially modulated charge produces a transverse space charge field E_{sc} which is perpendicular to the applied electric field E_a. If the interior field E_{sc} influences refractive index of azopolymer, the photorefractive grating in the command substrate can be recorded. This grating was not detected in our experiments. It may be caused by low efficiency of the electro-optic effect in our polymer. In LC cell, the field E_{sc} may cause photo-refractive effects in both command substrate and LC layer. Naturally, the effect is much more intensive in LC. The resulting electric field $E = E_{sc} + E_a$ forms a torque forcing LC director to reorient along E lines. As the field Ez is spatially modulated (both direction and magnitude), according to modulation of the density of charges, LC director is also spatially modulated. This mechanism, similar to classical photorefraction, was suggested and theoretically proven in [9,10].

In addition, one more reason should be mentioned. The charges generated in a command substrate may essentially modify LC anchoring energy, as discussed in references 21 and 22. In turn, the anchoring energy determines magnitude of the Frederiks threshold [13]. Hence, spatially modulated density of charges may cause spatial modulation of LC anchoring energy. As result, LC director can be spatially modulated at the action of external voltage close to Frederiks threshold. Beyond doubt, this fact should be taken into account to improve theory of grating mechanism.

The mechanism suggested allows simply explaining the grating characteristics. The threshold-like dependence $\eta(U)$ with the threshold voltage corresponding to Frederiks transition (Fig. 3) is in full agreement with the model discussed above. The η saturation and the following decrease for the voltages above the Frederiks threshold can be explained with saturation and subsequent "washing out" of the induced grating. The increase of η with the decreasing of 2θ (increasing of grating period Λ), shown in Figure 6, is typical for LC non-linear media. In frame of the photorefractive mechanism, growing of η with the increase of Λ can be explained with better separation of the electrical charges on azopolymer substrate. The tilt geometry for grating observation is required to enhance projection of LC director oriented in electric field on the polarization direction of the recording beams. In other words, this procedure helps to enhance sensitivity of our method to detect the grating recorded in LC.

CONCLUSIONS

In conclusion, holographic recording in LC cells based on azopolymer substrates is studied. The azopolymer films function both as photoaligning and photoconducting substrates. A grating induced in the cell in two-wave mixing experiment and observed in the electric field close to Frederiks transition is assumed to be caused by electro-optic effect in LC stipulated by spatially modulated charge in the azopolymer substrate. In this sense, the grating is recorded due to non-classical photorefractive mechanism. The high diffraction efficiency and the fairly high photosensitivity make studied system attractive for a number of advanced applications in the non-linear optical devices.

REFERENCES

[1] Eich, M., Wendorff, J. H., Reck, B., & Ringsdorf, H. (1987). Reversible digital and holographic optical storage in polymeric liquid crystals. *Macromol. Chem., Rapid Commun.*, *8*, 59–63.

[2] Dumont, M. & Sekkat, Z. (1992). Dynamical study of photoinduced anisotropy and orientational relaxation of azo dyes in polymeric films. Poling at room temperature. *Proceed SPIE*, *1774*, 188–199.

[3] Hvilsted, S., Andruzzi, F., & Ramanujam, P. S. (1992). Side-chain liquid crystalline polyesters for optical information storage. *Optics Letters*, *17*, 1234–1236.

[4] Natansohn, A., Rochon, P., Gosselin, J., & Xie, S. (1992). Azo polymers for reversible optical storage. *Macromolecules*, *25*, 2268–2273.

[5] Yaroshchuk, O., Kiselev, A., Zakrevskyy, Yu., Stumpe, J., & Lindau, J. (2001). Spatial reorientation of azobenzene side groups of a liquid crystalline polymer induced by linearly polarized light. *Eur. Phys. J E.*, *6*, 57–67.

[6] Ichimura, K., Susuki, Y., Seki, T., Hosoki, A., & Aoki, K. (1988). Reversible change in alignment mode of nematic liquid crystals regulated photochemically by "command surfaces" modified with an azobenzene monolayer. *Langmuir*, *4*, 1214–1216.

[7] Gibbons, W., Kosa, T., Palffy-Muhoray, P., Shannon, P. J., & Sun, S. T. (1995). Continuous gray-scale image storage using optically aligned nematic liquid crystals. *Nature*, *377*, 43–46.

[8] Miniewicz, A., Bartkiewicz, S., & Kajzar, F. (1998). On the dynamics of coherent amplification of light observed in liquid crystal panel with photoconducting polymeric layer. *Nonlinear Optics*, *19*, 157–175.

[9] Bartkiewicz, S., Matczyszyn, K., Miniewicz, A., & Kajzar, F. (2001). High gain of light in photoconducting polymer–nematic liquid crystal hybrid structures. *Optics Comm.*, *187*, 257–261.

[10] Bartkeiewicz, S., Miniewicz, A., & Kajzar, F. (2001). Photoconducting polymer – Nematic liquid crystal hybrid structures the promising choice for optical information processing. *Mol. Cryst. Liq. Cryst.*, *361*, 135–142.

[11] Kosa, T. & Palffy-Muhoray, P. (1996). Optically aligned liquid crystals: physics and applications. *Pure Appl. Opt.*, *5*, 595–602.

[12] Chen, S. H., Kuo, C. L., Wei, J. G., & Hao, C. W. (1992). Implementation and assessment of a tilt angle measurement system for liquid crystal cell: SPIE. *1815*, 194-205.

[13] Khoo, I. C. (1995). *Liquid Crystals Physical Properties and Nonlinear Optical Phenomena*, J. Wiley: New York.

[14] Gunter, P. & Huignard, J.-P. eds. (1988). *Photorefractive Materials and their Applications*, Springer Verlag: Berlin. vol. 1 and 2.

[15] Zeldovich, B., Pilipetski, I., Sukhov, A., & Tabiryan, N. (1980). Orientational optical non-linearity of liquid crystals. *JETP Lett.*, *31*, 263–267.

[16] Janossy, I., Csillag, L., & Lloyd, A. D. (1991). Temperature dependence of the optical Freedericksz transition in dyed nematic liquid crystals. *Phys. Rev. A.*, *44*, 8410–8413.

[17] Barnik, M. I., Zolot'ko, A. S., & Kitaeva, V. F. (1997). Interaction of light with a dye doped nematic liquid crystal. *JETP*, *84*, 1122–1130.

[18] Pinkevich, I., Reznikov, Yu., Reshetnyak, V., & Yaroshchuk, O. (1992). Conformational optical non-linearity of nematic liquid crystals. *Int. J. Nonlin. Opt, Phys.*, *1*, (3), 447–472.

[19] Yeh, P. ed. (1993). *Introduction to Photorefractive Nonlinear Optics*, Willey: New York.

[20] Nolte, D. ed. (1995). *Photorefractive effects and materials*, Kluwer Acad.Publ.: Boston.

[21] Blinov, L. M., Kabaenkov, A. Yu., & Sonin, A. A. (1989). Experimental studies of the anchoring energy of nematic liquid crystals. *Liq. Cryst.*, *5*, 645–661.

[22] Barbero, G., Evangelista, L. R., & Madhusudana, N. V. (1998). Effect of surface electric field on the anchoring of nematic liquid crystals. *Eur. Phys. J. B.*, *1*, 327–331.