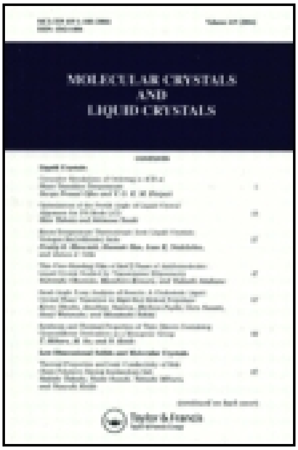


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Orientational Light Interaction with Nematic Liquid Crystal Doped with MEH-PPV Polymer

A. S. Zolot'ko [a], A. S. Averyushkin [a], V. F. Kitaeva [a], A. N. Lobanov [a], V. N. Ochkin [a], M. P. Smayev [a], A. G. Vitukhnovsky [a] & M. I. Barnik [b]
[a] P. N. Lebedev Physical Institute, Moscow, Russia
[b] A. V. Shubnikov Institute of Crystallography, Moscow, Russia

Version of record first published: 17 Oct 2011

To cite this article: A. S. Zolot'ko, A. S. Averyushkin, V. F. Kitaeva, A. N. Lobanov, V. N. Ochkin, M. P. Smayev, A. G. Vitukhnovsky & M. I. Barnik (2006): Orientational Light Interaction with Nematic Liquid Crystal Doped with MEH-PPV Polymer, Molecular Crystals and Liquid Crystals, 451:1, 41-52

To link to this article: http://dx.doi.org/10.1080/154214090960063

Mol. Cryst. Liq. Cryst., Vol. 451, pp. 41–52, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214090960063

Orientational Light Interaction with Nematic Liquid Crystal Doped with MEH-PPV Polymer

A. S. Zolot'ko
A. S. Averyushkin
V. F. Kitaeva
A. N. Lobanov
V. N. Ochkin
M. P. Smayev
A. G. Vitukhnovsky
P. N. Lebedev Physical Institute, Moscow, Russia

M. I. Barnik
A. V. Shubnikov Institute of Crystallography, Moscow, Russia

Nonlinear-optical properties of nematic liquid crystal 5CB doped with a small amount of high-molecular polymer MEH-PPV (poly[2-methoxy-5-(2′-ethylhexyl-oxy)-1,4-phenylenevinylene]) have been studied. This liquid crystalline system was shown to exhibit a negative nonlinearity due to the light-induced director reorientation away from the light-field direction.

Keywords: light-induced effects; nematic liquid crystals; optical nonlinearity; polymers

INTRODUCTION

Nematic liquid crystals (NLCs), owing to the combination of orientational ordering and mobility of their molecules, are extremely sensitive to external factors; in particular, to the influence of light fields.

This work was partially supported by the Russian Foundation for Basic Research [projects no. 04-02-17354, 05-02-17418 (A. S. Z., V. F. K., V. N. O., M. P. S., and M. I. B.), 04-02-17040, and 03-02-16817 (A. N. L. and A. G. V.)] and the federal programs "Integration," project no. B0049, and "Studies and Developments in Priority Areas of Science and Technology."

Address correspondence to A. S. Zolot'ko, P. N. Lebedev Physical Institute, Leninsky pr. 53, Moscow, 119991, GSP-1, Russia. E-mail: zolotko@sci.lebedev.ru

Thus, in focused beams (the waist $w \approx 50\,\mu m$) of continuous wave laser a Freedericksz transition threshold in transparent NLCs is attained at the beam power as low as $P \sim 10^{-1}$ W; that is, at the power density $S \approx 10^3$ W/cm^2 [1]. The corresponding orientational optical nonlinearity exceeds the Kerr nonlinearity of ordinary liquids by nine orders of magnitude [2].

An orienting effect of light on transparent NLCs is reduced to direct influence of the electric field of the light wave **E** on the molecular dipoles induced by the same field. As a consequence, the direction **n** is oriented parallel to **E** (in this case, the extraordinary refractive index is increased and, correspondingly, the optical nonlinearity is positive).

In NLCs doped with minor (0.1–1 wt%) amounts of light-absorbing dyes [3–8] or low-molecular polymers (molecular weight $M \sim 500$ [8], as well as in a light-absorbing nematic matrix [9], the orientational nonlinearity can be additionally enhanced by one–two orders of magnitude; in so doing, the director **n** can be rotated both toward and away from the light field **E**. (In the latter case the extraordinary refractive index decreases and the orientational nonlinearity is negative.)

At the present time, the mechanism of the light-induced director rotation in absorbing NLCs is not conclusively established. However, it is generally recognized that the torque is produced owing to an interaction of the ensemble of excited dye molecules (or excited molecules of a nematic matrix), which is characterized by a nonsymmetrical (with respect to the director **n**) orientational distribution, and the nonexcited molecules of the nematic matrix [10–13].

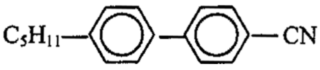
Orientational optical nonlinearities of NLC can be used for phase conjugation, light beam amplification, and so forth at low power density of light waves [14,15].

Thus, the search for new nonlinear liquid crystalline materials and the study of the physical mechanisms of their interaction with light field is a rather pressing problem.

We report a first observation of orientational optical phenomena in NLCs containing an admixture of an absorbing high-molecular polymer. For such a polymer, we used MEH-PPV (poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]), molecular weight $M \sim 10^6$.

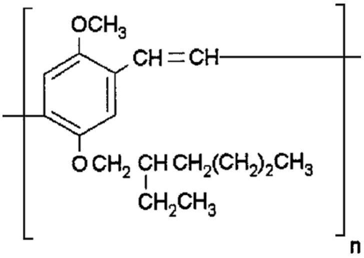
EXPERIMENTAL SAMPLES AND TECHNIQUE

Pentylcyanobiphenyl (5CB)



is transparent in visible region and was used as a nematic host. 5CB exhibits a nematic phase in the temperature range $22°\mathrm{C} < t < 35°\mathrm{C}$.

Conjugated polymer MEH-PPV



(absorption-band peak at $\lambda_{\mathrm{m}} = 497\,\mathrm{nm}$) is a synthetic polymeric molecule with a backbone of conjugated carbon double bouds. Kinks, bends, and chemical defects break the full conjugation of the backbone into the segments of quasi-independent chromophores [16] of different lengths and orientations. Depending on the nature of matrix and solvent, polymeric molecules have different conformations, varying from tight coils to extended structures. Optical absorption is strongly dependent upon the molecular conformations and aggregation of polymeric chains. These chains can form aggregates with either the other molecules or the segments of the same molecule (self-aggregation). Even a single MEH-PPV molecule showed the presence of strong coupling between thousands of chromophore segments, as shown by spectroscopic studies [17].

Although the orientational ordering of low-molecular ($M \sim 500$) impurities in a liquid crystalline host has been extensively studied [18], this is not the case for the impurities of high-molecular ($M \sim 1000000$) polymeric molecules. The way the interaction of chromophore segments and LC host molecules is changed under polymer excitation is unknown. One can only assume that this interaction changes significantly within several monomer units, because the excitonic localization length of an isolated MEH-PPV molecule involves 10–17 monomers [19].

To mix the nematic and polymer, both components were dissolved in chloroform (the concentration of MEH-PPV (Aldrich) was 0.16 wt% with respect to 5CB). The mixture obtained upon chloroform evaporation was not homogeneous. Visually, this consisted of two fractions being different in color intensity. The less-colored fraction was mainly used to prepare the samples.

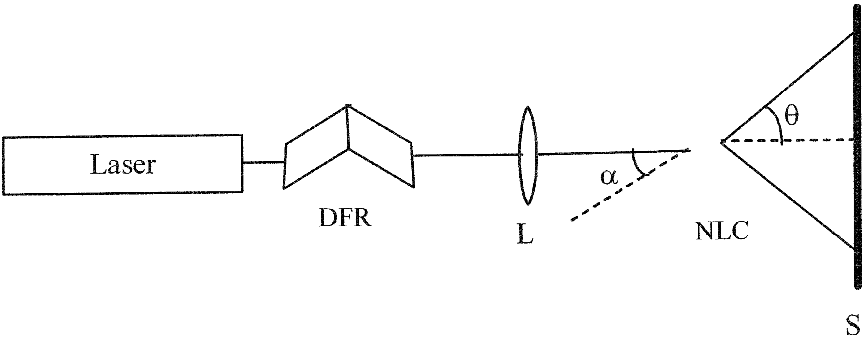


FIGURE 1 Schematic representation of the experimental setup: DFR is double Fresnel rhomb, L is focusing lens, NLC is nematic liquid crystal, S is screen, α is the angle of incidence of the light beam on NLC, and θ is the angle of nonlinear divergence of the aberrational pattern.

Homeotropic and planar NLC cells with the thickness $L = 100\,\mu m$ were used. Planar alignment was produced by buffing thin ($\sim 500 - 1000\,nm$) polyimide layers deposited on glass plates, which were previously coated with electroconductive indium tin oxide layers (ITO). Homeotropic alignment was achieved by the deposition of thin ($\sim 50\,nm$) films of chromium stearylchloride.

Figure 1 shows the schematic representation of the experimental setup. As a light source we used solid state ($\lambda = 532\,nm$), argon ($\lambda = 458$, 477, 488, 501, or 515 nm), or argon–krypton ($\lambda = 647\,nm$) lasers. Most experiments were performed at the wavelengths $\lambda = 515$ and 532 nm. A light beam was focused into a NLC cell by a lens with the focal length $f = 18\,cm$. A double Fresnel rhomb was used to rotate the polarization plane of the light beam. The plane of the liquid crystal layer was vertical; the unperturbed director $\mathbf{n}_0$ was in the horizontal plane. The angle of the light incidence on a NLC cell could be changed by rotating the cell about the vertical axis (the angle α is taken positive for counterclockwise rotation and negative in the opposite case).

The light-induced director reorientation was accompanied by an aberrational self-action of the light beam; as a consequence, a system of rings was observed on a screen placed behind the NLC cell. The number of these rings allows one to evaluate the director rotation angle [20,21].

To determine the sign of self-action, we used the method [6] based on the observation of the aberrational pattern transformation appearing after a rather fast shift of the NLC cell relative to the light beam.

In the experiment, we measured the dependences of the number of aberrational rings N on the light beam power, the angle φ of the polarization rotation, and the low-frequency voltage U applied to the cell.

EXPERIMENTAL RESULTS

Interaction of Light Beam with Homeotropic Cell

No aberrational pattern was observed at a normal light incidence on the cell.

At oblique light incidence on the NLC cell (for all wavelengths in the range 458–647 nm, $\alpha = 50^\circ$), an aberrational pattern consisting of concentric rings developed on the screen during a time interval $t \sim 7-10\,\mathrm{s}$ (Fig. 2a). The relaxation time of the ring pattern (determined with the aid of a probe beam) was $\tau_R = 10-15\,\mathrm{s}$. Figure 3 (curve 1) shows the dependence of the number of aberrational rings on the light power P at $\lambda = 515\,\mathrm{nm}$. It is evident that increasing P results in an increase of N up to a certain limit value $N_{\max} = 6$.

Application of an external low-frequency electric field ($U = 2.5\,\mathrm{V}$, $\nu = 3\,\mathrm{kHz}$) to the NLC cell resulted in the collapse of the pattern.

The determination of the self-action sign showed that in the blue–green spectral range, 458–532 nm, the self-defocusing is observed, whereas at the red line $\lambda = 647\,\mathrm{nm}$ the self-focusing of the light beam is developed.

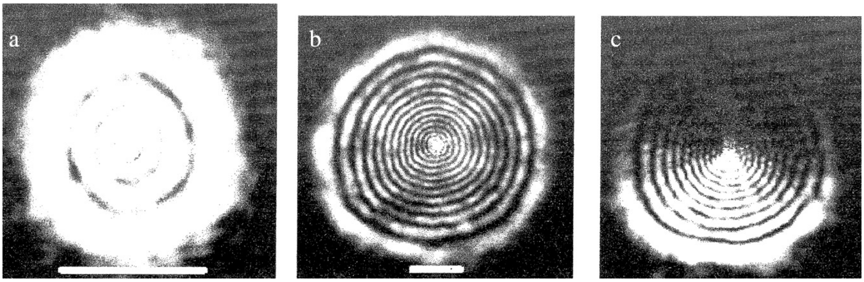


FIGURE 2 Aberrational pattern formed in the light beam upon passing through (a) homeotropic and (b, c) planar cells with 5CB + 0.16 wt% MEH-PPV ($\lambda = 515\,\mathrm{nm}$, $\mathrm{P} = 2\,\mathrm{mW}$, $\alpha = 50^\circ$): (a, b) the cell is stationary and (c) in $\sim 1\,\mathrm{s}$ after an upward shift of the cell with respect to the light beam. White segments (a, b) correspond to 0.05 rad. The increase in the intensity of the lower part of the aberrational pattern (and the corresponding decrease in the intensity of the upper part) (c) implies the negative sign of the self-action (self-defocusing).

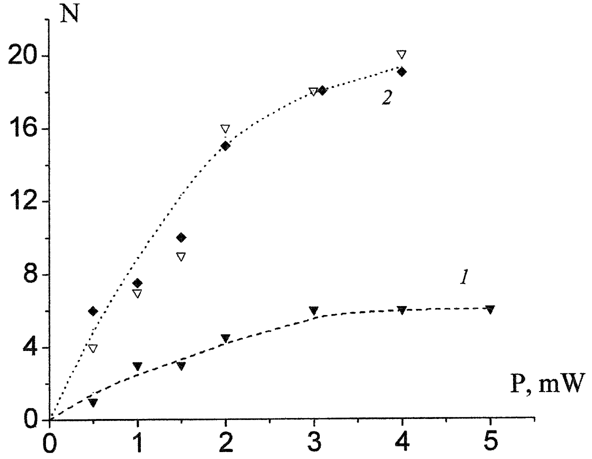


FIGURE 3 Experimental dependences of the number N of aberrational rings N on the light power P for homeotropic (curve 1,◆) and planar (curve 2, $\alpha = +50°$, ▽, and $-50°$, ▼) cells with 5CB + 0.16 wt% MEH-PPV ($\lambda = 515$ nm).

Figure 4 (curve 1) shows the dependence of the number of aberrational rings N on the angle φ of the polarization plane rotation (taken with respect to horizontal plane) of the beam incident on the NLC cell.

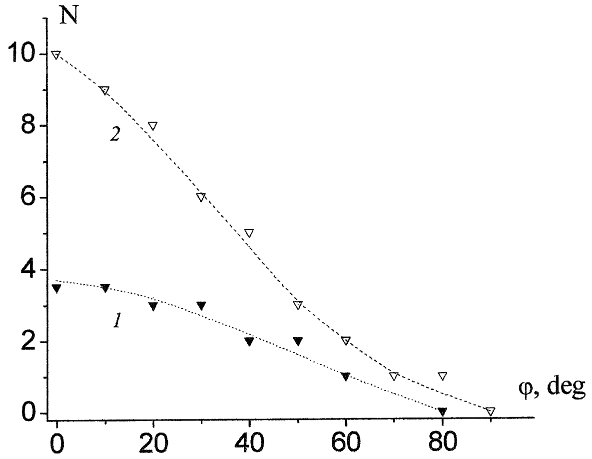


FIGURE 4 Experimental dependences of the number N of aberrational rings on the angle of the polarization plane rotation φ for homeotropic (curve 1, ◆) and planar (curve 2, ▽) cells with 5CB + 0.16 wt% MEH-PPV ($\lambda = 515$ nm, P = 1.5 mW, $\alpha = 50°$).

It is seen that the aberrational pattern collapses (to $N = 0$) as one goes from the horizontal ($\varphi = 0°$, extraordinary wave) to vertical ($\varphi = 90°$, ordinary wave) polarization. In the course of the polarization plane rotation, the rings retain horizontal polarization and a vertically polarized spot appears in the center of the aberrational pattern.

The order of magnitude of the time intervals characteristic of the development and relaxation of the aberrational pattern [9] and its suppression by the external field testify that the ring pattern results from the director reorientation. This is also evidenced by the polarization dependence of the number of the aberrational rings. In fact, if the thermal mechanism of the light self-action were the case, the polarization rotation would not cause the disappearance of the aberrational rings.

Interaction of Light Beam with Planar Cell

At normal incidence of the light beam, aberrational rings were formed practically instantaneously (e.g., at $\lambda = 515\,\text{nm}$ and P = 2 mW the aberrational ring number was $N = 2$). The rapid development of the aberrational pattern indicates a thermal (and not the orientational) mechanism of the light self-action in this case.

At oblique light incidence on the planar NLC cell (for all wavelengths in the range 458–647 nm, $\alpha = 50°$), the aberrational pattern (Fig. 2b) was formed with the same time behavior as in the case of the homeotropic cell. The ring number N increased with increasing P (Fig. 3, curve 2). One can see from Fig. 3 that at equal light-beam powers the N value for the planar cell is greater than that for the homeotropic one. The direction of the light beam incidence (i.e., the sign of the angle α) does not affect the number of aberrational rings.

The influence of external low-frequency field results in a more complex phenomenon than for the homeotropic cell (a simple suppression of the light-induced reorientation). As the voltage U increases (see Fig. 5), the ring number N changes nonmonotonically, peaking ($N = N_{\max}$) at a certain voltage value $U_{\max} \sim 0.7\,\text{V}$. The $N_{\max}$ value increases with P. It might be good to point out that at $U = 0$ and $P = 2\,\text{mW}$ the value $N = 2$ corresponds, as stated previously, to the thermal self-action; at higher U, the orientational mechanism is dominant [this is evidenced by the slowness ($\sim 10\,\text{s}$) of the aberrational pattern formation].

In common with the homeotropic cell, the self-defocusing was observed in the blue–green spectral range (458–532 nm) and the self-focusing at $\lambda = 647\,\text{nm}$.

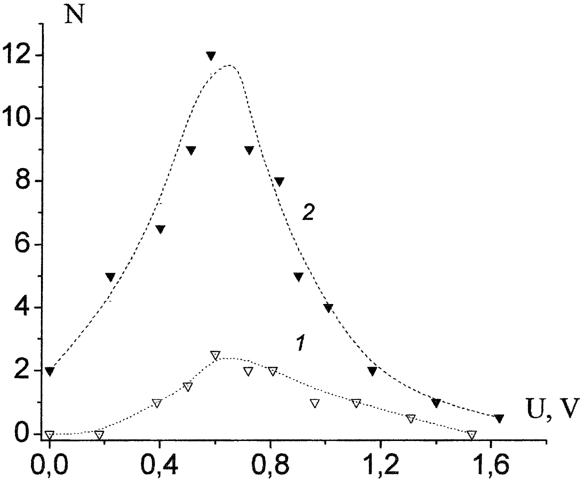


FIGURE 5 Experimental dependences of the number N of aberrational rings on external low-frequency ($\nu = 3\,\mathrm{kHz}$) voltage U for planar cell with 5CB + 0.16 wt% MEH-PPV at normal incidence ($\lambda = 515\,\mathrm{nm}$): P = 0.5 mW (curve 1, ▽) and 2 mW (curve 2, ▼).

The nonmonotonic character of the dependence $N(U)$ (Fig. 5) can be qualitatively explained as follows. The increasing low-frequency electric field turns the planar director orientation in the NLC bulk into the homeotropic one. In so doing, the angle between the light field **E** and director **n** is increased, which is first favorable for the light-induced orientation (an increase in N). At sufficiently high voltage U, the director becomes oriented along the low-frequency electric field (normal to the NLC surfaces) and the light-induced orientation does not occur at all.

Notice that the type of the $N(U)$ dependence also rules out the thermal mechanism of the aberrational pattern development. Indeed, an increase in the angle between **n** and **E** decreases both the absorption (i.e., the NLC heating) and the magnitude of the temperature derivative of the extraordinary refractive index [22]. This would result in decrease of the ring number N (and not in the experimentally observed increase).

The dependence of N on the angle φ of the polarization-plane rotation of the light beam incident on planar cell (Fig. 4, curve 2) is similar to that for the homeotropic cell.

Thus, the results obtained show that in the planar aligned cell (as in the homeotropic one) the light-induced director reorientation is observed.

DISCUSSION

At first, we dwell on the spectral dependence of the sign of the observed orientational self-action (self-defocusing in the range $\lambda = 458$–$532\,\text{nm}$ and self-focusing at $\lambda = 647\,\text{nm}$). As was mentioned previously, the orientational self-defocusing corresponds to the director reorientation *away from the light-field direction.* Such a rotation (further referred to as the negative one) can only stem from changing the intermolecular forces at the orientationally selective excitation of the chromophore segments. The self-focusing at the red line (where no polymer excitation occurs) is due to the direct influence of the light field on the induced dipoles, which is inherent to transparent NLCs.

It is pertinent to note that the quantitative study of the orientational nonlinearity of the polymer–nematic system is beyond the scope

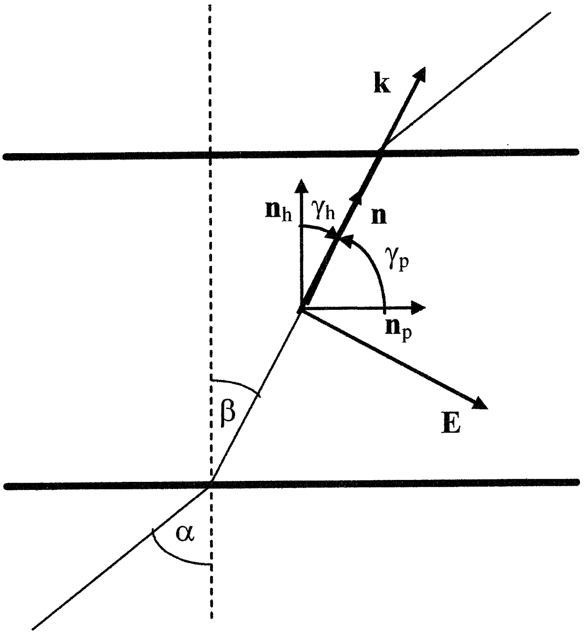


FIGURE 6 Geometry of orientational influence of a light beam on homeotropic and planar NLCs: **E**, **k**, α, β are the electric field, wave vector, angle of incidence, and angle of refraction of the light, respectively; $\mathbf{n}_h$ and $\mathbf{n}_p$ are the unperturbed director for initial homeotropic and planar orientation of the cell, respectively; **n** is the director rotated normally to the light field **E**; $\gamma_h = \beta$ and $\gamma_p = 90° - \beta$ are the maximum possible angles of the light-induced director rotation in homeotropic and planar cells, respectively.

of this publication. Such a study requires a consideration of the lightwave decay due to absorption and the knowledge of the exact concentration of the polymer in nematic host.

Now consider why in the spectral range of negative rotation the number of the aberrational rings N for the planar cell is greater than that for the homeotropic one. This difference is explained (see Fig. 6) by the fact that in the first case the possible angle γ_{p} of the director rotation away from the light field **E** (and with it the magnitude of the possible light-induced change in the refractive index) is greater than the respective angle γ_{h} in the second case.

As already noted, for the light absorption to result in the director rotation, and ensemble of excited molecules with the nonsymmetrical (with respect to the director **n**) distribution must be generated. This is only possible if an orientational "spread" is inherent in the nonexcited segments.

To elucidate the character of the polymeric-chain ordering by the nematic host, we measured the transmission of the extraordinary and ordinary waves at a normal incidence of light on the planar aligned cell. The measurements were performed on a Specord M40 spectrograph supplied with a polaroid to produce a linearly polarized radiation. From the data obtained, the absorption coefficients at the MEH-PPV absorption maximum were estimated to be $\alpha_{\parallel} = 70\,\mathrm{cm}^{-1}$ and $\alpha_{\perp} = 45\,\mathrm{cm}^{-1}$ for the extraordinary and ordinary waves, respectively. The absorption dichroism implies that chromophore segments of the polymeric chains of MEH-PPV macromolecules acquire a preferred orientation, induced by NLC host.

For a quantitative estimation of the degree of the polymer orientation we use a well-known relation [18] for the order parameter S_{a} of light-absorbing molecules,

$$S_{\mathrm{a}} = \frac{N_{\mathrm{D}} - 1}{N_{\mathrm{D}} + 1}\left(1 - \frac{3}{2}\sin^2\beta_{\mathrm{a}}\right)^{-1}, \tag{1}$$

where N_{D} is the dichroic ratio (equal to $N_{\mathrm{D}} = \alpha_{\parallel}/\alpha_{\perp}$), and β_{a} is the angle the absorption oscillator makes with the longer molecular axis (in our case, with the direction of the polymer segments). Assuming that $\beta_{\mathrm{a}} = 0$ and substituting in Eq. (1) the previous values of the absorption coefficients, we get $S_{\mathrm{p}} \sim 0.15$.

Thus, the degree of the polymer segment orientation by the nematic host is not high. This property is favorable for the formation of an orientationally nonsymmetrical distribution of polymeric segments and, hence, for the manifestation of optical orientational phenomena.

A specific feature of the composite liquid crystalline system under study is that the rotational motion of the chromophore segments is suppressed by their inclusion in the long polymer backbone. This property may be advantageous for increasing orientational nonlinearities. In fact, the concentration of excited molecules of a dye or, in the case of polymers, the excited segments of a polymer chain, which retain the the memory of the exciting-light polarization and produce the torque on the director **n**, is proportional to the minimum of the two characteristic times: (1) the lifetime of the excited state τ_e and (2) the rotational diffusion time τ_D. For ordinary dye molecules, $\tau_D \sim 10^{-9} - 10^{-8}$ s [11]. For long polymer chains, rotational diffusion should be suppressed ($\tau_D = \infty$). Hence, at $\tau_e > 10^{-8}$ s the orientational nonlinearity may be higher than that featured in the case of conventional low-molecular dyes.

CONCLUSIONS

In this work we studied the nonlinear optical properties of a nematic host doped with a high-molecular polymer and observed the orientational nonlinearity due to the light absorption by polymeric chromophore segments.

REFERENCES

[1] Zolot'ko, A. S., Kitaeva, V. F., Kroo, N., Sobolev, N. N., & Chillag, L. (1980). *JETP Lett.*, *32*, 158.

[2] Zel'dovich, B. Ya., Pilipetskii, N. F., Sukhov, A. V., & Tabiryan, N. V. (1980). *JETP Lett.*, *31*, 263.

[3] Janossy, I. & Lloyd, A. D. (1991). *Mol. Cryst. Liq. Cryst.*, *202*, 77.

[4] Janossy, I. & Kosa, T. (1992). *Opt. Lett.*, *17*, 1183.

[5] Marrucci, L., Paparo, D., Maddalena, P., Massera, E., Prudnikova, E., & Santamato, E. (1997). *J. Chem. Phys.*, *107*, 9783.

[6] Kitaeva, V. F., Zolot'ko, A. S., & Barnik, M. I. (2000). *Mol. Materials*, *12*, 271.

[7] Kreuzer, M., Hanisch, F., Eidenschink, R., Paparo, D., & Marrucci, L. (2002). *Phys. Rev. E*, *88*, art. no. 013902.

[8] Zhang, H., Shino, S., Kanazava, A., Tsutsumi, O., Shiono, T., & Ikeda, T. (2002). *J. Appl. Phys.*, *91*, 5558.

[9] Zolot'ko, A. S., Kitaeva, V. F., & Terskov, D. B. (1994). *JETP*, *79*, 931.

[10] Janossy, I. (1994). *Phys. Rev. E*, *49*, 2957.

[11] Marrucci, L. & Paparo, D. (1997). *Phys. Rev. E*, *56*, 1765.

[12] Palffy-Muhoray, P. & Weinan, E. (1998). *Mol. Cryst. Liq. Cryst.*, *320*, 193.

[13] Zolot'ko, A. S. (1998). *JETP Lett.*, *68*, 437.

[14] Khoo, I. C., Diaz, A., Ding, J., Chen, K., & Zhang, Y. (2003). *J. Nonlinear Opt. Phys. Materials*, *12*, 277.

[15] Ikeda, T. (2003). *J. Mater. Chem.*, *13*, 2037.

[16] Huser, T. & Yan, M. (2001). *J. Photochemistry Photobiology A: Chemistry*, *144*, 43.

[17] Vanden Bout, D. A., Yip, W. T., Hu, D., Swager, T. M., & Barbara, P. F. (1977). *Science*, *277*, 1074.

[18] Blinov, L. M. (1983). *Electro- and magneto-optics of liquid crystals*. Wiley: Chichester.

[19] Woo, H. S., Lhost, O., Graham, S. C., Bradley, D. D. C., Friend, R. H., Quattrocchi, C., Bredas, J. L., Schenk, R., & Mullen, K. (1993). *Synth. Met.*, *59*, 13.

[20] Zolot'ko, A. S., Kitaeva, V. F., Sobolev, N. N., & Sukhorukov, A. P. (1981). *JETP*, *54*, 496.

[21] Zolot'ko, A. S., Kitaeva, V. F., Kuyumchyan, V. A., Sobolev, N. N., & Sukhorukov, A. P. (1982). *JETP Lett.*, *36*, 80.

[22] Hsiung, H., Shi, L. P., & Shen, Y. R. (1984). *Phys. Rev. A*, *30*, 1453.