

# Light-induced director reorientation in NLC doped with high-molecular polymer

A.S. Zolot'ko<sup>\*a</sup>, A.S. Averyushkin<sup>a</sup>, V.F. Kitaeva<sup>a</sup>, A.N. Lobanov<sup>a</sup>, V.N. Ochkin<sup>a</sup>, M.P. Smayev<sup>a</sup>,  
A.G. Vitukhnovsky<sup>a</sup>, and M.I. Barnik<sup>b</sup>

<sup>a</sup>P.N. Lebedev Physical Institute, Leninsky pr. 53, Moscow, 119991, Russia

<sup>b</sup>A.V. Shubnikov Institute of Crystallography, Leninsky pr. 59, Moscow, 117333, Russia

## ABSTRACT

Light interaction with nematic liquid crystals doped with high-molecular polymer MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]) has been studied. The director reorientation away from the light field was found within the absorption band of the polymer. The reorientation is explained by the appearance of the torque due to changing the intermolecular forces between the polymer macromolecules and nematic-host molecules under polymer excitation by light absorption.

**Keywords:** nematic liquid crystals, high-molecular polymers, light-induced phenomena, orientational optical nonlinearity, light self-action

## 1. INTRODUCTION

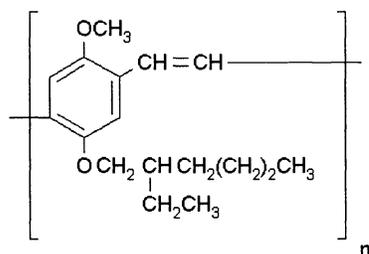
Transparent nematic liquid crystals (NLCs) are very sensitive to the orienting influence of light field [1, 2]. In NLCs doped with small amounts of light-absorbing dyes [3-8] and low-molecular polymers [9], the orientational optical nonlinearity can be additionally increased by two orders of magnitude. These nonlinearities can be used for phase conjugation, light beam amplification, etc., at low power density of light waves [10, 11], which stimulates the search for new nonlinear-optical liquid crystalline materials.

The aim of the present work is to study the interaction of light and NLC doped with a high-molecular polymer.

## 2. EXPERIMENTAL

The material under study was pentylcyanobiphenyl (5CB) doped with high molecular polymer poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) (the polymer concentration was 0.16 wt %). 5CB is transparent in visible region and has a nematic phase in the temperature range  $24^{\circ}\text{C} < t < 35^{\circ}\text{C}$ .

Conjugated polymer MEH-PPV (absorption-band peak at  $\lambda_m = 497 \text{ nm}$ )



is a synthetic polymeric molecule with a backbone of conjugated carbon double bonds. Kinks, bends and chemical defects break the full conjugation of the backbone into the segments of quasi-independent chromophores [12] of different lengths and orientations. Optical absorption is strongly dependent upon the molecular conformations and

\* zolotko@sci.lebedev.ru; phone 7-095-1322604; fax 7-095-1357880.

aggregation of polymeric chains. Even a single MEH-PPV molecule showed the presence of strong coupling between thousands chromophore segments, as shown by spectroscopic studies [13].

While the light orientational effect in liquid crystalline host doped with low-molecular ( $M \sim 1000$ ) impurities has been extensively studied, it is not the case for 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 all the more unknown.

Experiments were performed on planar and homeotropic cells with the thickness  $L = 100 \mu\text{m}$ . The glass plates of the cells were coated with ITO, which allowed us to apply an external low-frequency electric field.

The light sources were a solid-state ( $\lambda = 532 \text{ nm}$ ), argon ( $\lambda = 458, 477, 488, 501$  or  $515 \text{ nm}$ ), or argon–krypton ( $\lambda = 647 \text{ nm}$ ) lasers. Most experiments were performed at the wavelengths  $\lambda = 515$  and  $532 \text{ nm}$ . A light beam was focused into the liquid crystal cell by a lens with 18-cm focal length. The linear polarization of a laser beam could be rotated by a double Fresnel rhomb. The NLC cell plane was vertical; the unperturbed director  $\mathbf{n}_0$  was in horizontal plane. The angle of the light incidence could be changed by rotating the cell about the vertical axis (for definiteness, the angle  $\alpha$  is taken positive for counterclockwise rotation and negative in the opposite case).

The light-induced director reorientation is known to be accompanied by a formation of ring pattern in the transmitted beam (the number of aberrational rings being related to the director reorientation angle) [14, 15].

We measured the dependences of the number of aberrational rings  $N$  on the light beam power  $P$ , the angle  $\varphi$  between the light polarization direction and the horizontal plane, and the low-frequency voltage  $U$  applied to the cell. The sign of the self-action (self-focusing or self-defocusing) was determined by the method [7] based on the observation of the aberrational-pattern transformation upon a rather fast shift of the NLC cell relative to the light beam.

### 3. RESULTS AND DISCUSSION

At oblique light incidence on the *planar* NLC cell (for all wavelengths from the range  $458 - 647 \text{ nm}$ ,  $\alpha = 50^\circ$ ), the aberrational pattern (Fig. 1) was formed during a time interval  $t \sim 7-10 \text{ s}$ . The relaxation time of the ring pattern (determined with the aid of a probe beam) was  $\tau_R = 10 \div 15 \text{ s}$ . These times are typical of orientational processes. The ring number  $N$  increased with increasing  $P$  (Fig. 2). The direction of the light beam incidence (i.e., the sign of angle  $\alpha$ ) doesn't affect the number of aberrational rings.

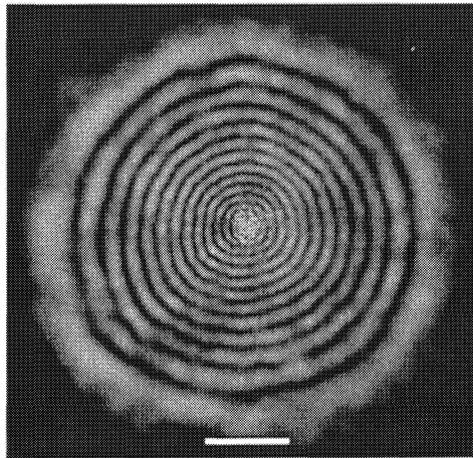


Fig. 1. Aberrational pattern formed in the light beam passed through planar cells with 5CB + 0.16 wt % MEH-PPV ( $\lambda = 515 \text{ nm}$ ,  $P = 2 \text{ mW}$ ,  $\alpha = 50^\circ$ ). White segment corresponds to  $0.05 \text{ rad}$ .

Figure 3 shows  $N$  vs. the angle  $\varphi$  of the polarization plane rotation (with respect to horizontal plane) of the beam incident on the NLC cell. It is evident that the aberrational pattern collapses (to  $N = 0$ ), as one goes from the horizontal (extraordinary wave) to vertical (ordinary wave) polarization. Such a dependence confirms the orientational nature of

the self-action—if the thermal mechanism of the light self-action took place, the polarization rotation would not cause the disappearance of the aberrational rings.

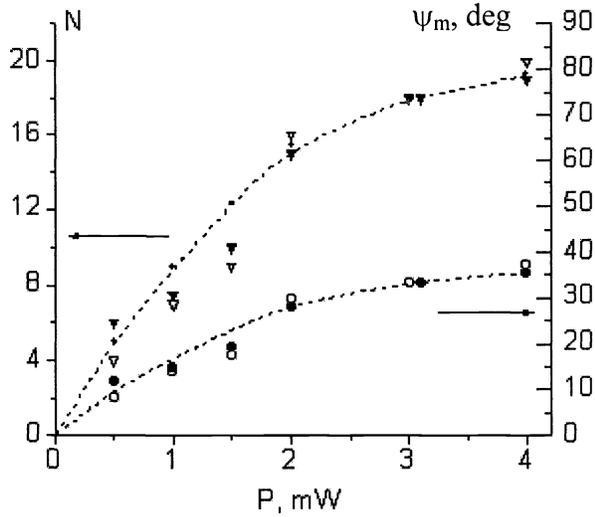


Fig. 2. The dependences of the measured number  $N$  of aberrational rings  $N$  (B, X) and the calculated angle  $\psi_m$  (., -) of the light induced director reorientation on the light-beam power  $P$  for planar cell with 5CB + 0.16 wt % MEH-PPV for  $\alpha = + 50^\circ$  (X,-) and  $- 50^\circ$  (B,,) ( $\lambda = 515$  nm).

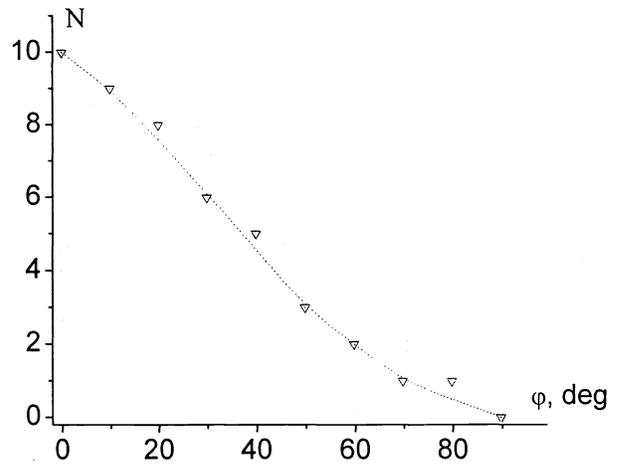


Fig. 3. Experimental dependences of the number  $N$  of aberrational rings on the angle of the polarization plane rotation  $\phi$  for planar cell with 5CB + 0.16 wt % MEH-PPV ( $P = 1.5$  mW,  $\lambda = 515$  nm,  $\alpha = 50^\circ$ )

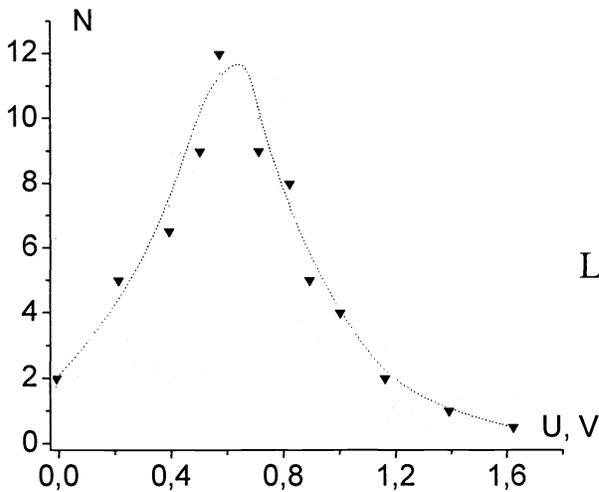


Fig. 4. Experimental dependence of the number  $N$  of aberrational rings on external low-frequency ( $\nu = 3$  kHz) voltage  $U$  for planar cell with 5CB + 0.16 wt % MEH-PPV at normal incidence ( $\lambda = 515$  nm,  $P = 2$  mW).

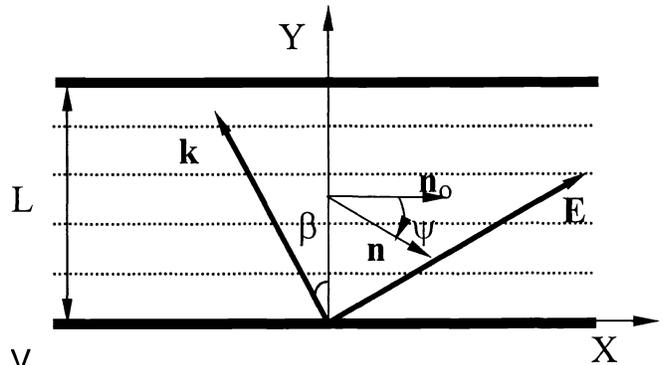


Fig. 5 Geometry of the orientational influence of a light beam on planar NLC:  $\mathbf{E}$ ,  $\mathbf{k}$ ,  $\beta$  are the electric field, wave vector, and angle of refraction of the light, respectively;  $\mathbf{n}_0$  is the unperturbed director for initial planar orientation of the cell; and  $\mathbf{n}$  is the director rotated away from the light field  $\mathbf{E}$ .

At normal incidence of the light beam, the stable aberrational pattern in blue-green range were formed in less than 0.1 s (e.g., at  $\lambda = 515$  nm and  $P = 2$  mW the aberrational-ring number was  $N = 2$ ). Such a rapid development of the aberrational pattern indicates a thermal (and not the orientational) mechanism of the light self-action in this case.

Application of the low-frequency voltage increases first the ring number  $N$  (see Fig. 4). Then, the  $N$  value approaches maximum ( $N = N_{\max}$ ) at a certain voltage value  $U_{\max} \sim 0.7$  V, and decreases. It might be well to point out that at  $U = 0$  the value  $N = 2$  corresponds, as stated above, to the thermal self-action; at higher  $U$ , the orientational mechanism is dominant (this is evidenced by the slowness ( $\sim 10$  s) of the aberrational pattern formation).

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  $\lambda = 647$  nm the self-focusing of the light beam is developed.

In the case of the homeotropic cell, the orientational self-action with the same spectral dependence was also observed. In this case, however, the number of aberrational ring was lower than for planar cell by a factor of about 3. Application of low-frequency field suppressed monotonically the aberration pattern.

It is known that the orientational self-defocusing corresponds to the director reorientation away from the light-field direction (see Fig. 5). Such sense of rotation (referred to as the negative one) can only be related to the processes of the light absorption by molecules and their excitation. The self-focusing at the red line is related to the absence of the excitation away from the absorption band. In this case, the positive (toward the light field  $\mathbf{E}$ ) reorientation occurs, which is inherent to transparent NLCs.

As mentioned above, one can estimate the director rotation angle from the number of aberrational rings  $N$ . To this end, we shall use the relation:

$$N = \frac{|S_{\text{NL}}|}{2\pi}. \quad (1)$$

In the Cartesian coordinate system  $XY$  shown in Fig. 5 the nonlinear phase shift  $S_{\text{NL}}$  is:

$$S_{\text{NL}} = \frac{2\pi}{\lambda \cos \beta} \int_0^L \Delta n(y) dy, \quad (2)$$

where  $\Delta n(y)$  is the light-induced change in the refractive index of the extraordinary wave equal to

$$\Delta n(y) = \frac{\sqrt{\varepsilon_{\perp} \varepsilon_{\parallel}}}{\sqrt{\varepsilon_{\perp} \cos^2(\beta + \psi) + \varepsilon_{\parallel} \sin^2(\beta + \psi)}} - \frac{\sqrt{\varepsilon_{\perp} \varepsilon_{\parallel}}}{\sqrt{\varepsilon_{\perp} \cos^2 \beta + \varepsilon_{\parallel} \sin^2 \beta}}, \quad (3)$$

where  $\beta$  is the refraction angle, while  $\psi$  is the angle of the light-induced director reorientation (see Fig. 5). Assuming the harmonic dependence of the angle  $\psi$ ,

$$\psi(y) = \psi_m \sin(\pi y / L), \quad (4)$$

expanding (3) in small parameter  $\delta n = \varepsilon_{\parallel}^{1/2} \Delta \varepsilon / 2\varepsilon_{\perp}$ , and substituting the resulting expression into (2) and (1) we finally arrive at the relation between the angle of the director rotation at the beam axis  $\psi_m$  and the number of the aberrational rings of the self-defocusing:

$$N = \frac{\delta n L}{2\lambda \cos \beta} [(1 - J_0(2\psi_m)) \cos 2\beta - E_0(2\psi_m) \sin 2\beta], \quad (5)$$

where  $J_0(2\psi_m)$  is the zero order Bessel function and  $E_0(2\psi_m)$  is the zero order Weber function. The dependence  $\psi_m(P)$  calculated by (5) from the experimental data presented in Fig. 2 is shown on the same figure.

As is known [16-19], for the light-induced director rotation in absorptive NLCs to take place, an ensemble of excited molecules with the nonsymmetrical (with respect to the director  $\mathbf{n}$ ) orientational distribution must be generated. This is only possible if the polymer segments in a nematic host are characterized by an orientational “spread”.

To determine the polymeric-chain ordering, we measured the transmission of the extraordinary and ordinary waves at a normal incidence of light on the planar cell. The absorption coefficients at the MEH-PPV absorption maximum were estimated to be  $\alpha_{\parallel} = 70 \text{ cm}^{-1}$  and  $\alpha_{\perp} = 45 \text{ cm}^{-1}$  for 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. However, the ratio  $\alpha_{\parallel} / \alpha_{\perp} \approx 1.5$  (and with it the degree of polymeric chain ordering), is rather low, as compared with ordinary dichroic dyes. Low degree of the polymeric ordering may be favorable for manifestation of orientational nonlinearity.

Let us discuss now the specific mechanism of the light-induced reorientation in high-molecular polymer doped nematics.

For low-molecular molecules, studies [16-18] related the light induced director orientation with the occurrence of the torque due to a change in the mean field (Maier-Saupe) potential and the rotation of excited-dye molecules. In [19], this orientation was explained by the torque produced due to the change in the noncentral potential of the van der Waals interaction under excitation of absorbing dye molecules and the anisotropy of the correlation function of dye and nematic-host molecules.

In the case of high-molecular polymers, the rotation of the excited segments must be greatly suppressed owing to their incorporation in the polymeric backbone. Therefore, we believe that the mechanism proposed in [19] is responsible for the observed orientational effect.

#### 4. CONCLUSIONS

We studied the interaction of light wave and NLC doped with high-molecular polymer MEH-PPV. The light-induced director reorientation away from the light-wave electric field was observed within the absorption band of the polymer. This reorientation is explained by changing the intermolecular forces under polymeric-chain excitation and the anisotropy of orientational correlation function.

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