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Light-Induced Orientation Transition in Nematic Liquid Crystalline Polymer

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Abstract—Optical orientation in transparent nematic liquid crystalline polymer (NLCP) was observed for the first time. In NLCP with dye dopant, the light-induced second-order orientation transition being an analogue of the Freedericksz transition in low-frequency fields is found. The transition threshold is ~10 μW which is lower than the threshold of the light-induced Freedericksz transition in low-molecular nematics by four orders of magnitude and is lower than the characteristic value for low-molecular nematics with dye dopant by two orders of magnitude.

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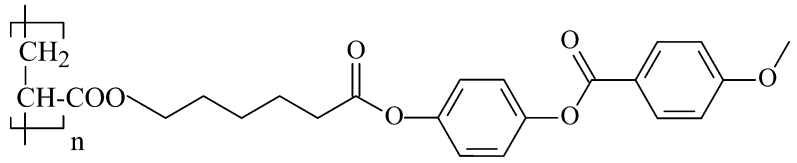
Introduction. In nematic liquid crystals (NLCs), the rotation of the director (unit vector characterizing the preferred orientation of molecules) occurs under a low-frequency electric or magnetic field [1]. The rotation is caused by the torque proportional to the anisotropy of permittivity or permeability. If the reorientation occurs under action of the field which is perpendicular or parallel to the NLC director, the director reorientation has a threshold nature; this case is referred to as the Freedericksz transition. The Freedericksz transition can be considered as the second-order orientational phase transition; in this case, the order parameter is the director rotation angle, and the acting variable (temperature analogue) is the external field [2]. The NLC director reorientation and threshold transition are also observed under a light field [3, 4]. The optical orientation mechanism in transparent NLCs is the orienting influence of light on induced dipoles. In dye-doped NLCs, a mechanism of optical orientation appears, which is associated with a change in intermolecular forces upon excitation of dye molecules [5–7]. In this case, the highest efficiency of optical orientation, characterized by the ratio of the torque amplification factor in comparison with the case of transparent NLC to the crystal absorption, was achieved for a polymeric absorbing additive [8].

For the nematic phase of liquid crystalline polymers, the director reorientation effects, including the threshold transition, were observed only for magnetic and low-frequency electric fields [9, 10]. At the same time, similar orientation effects upon exposure to light are of doubtless interest. First, rotational motion of chromophores in such a medium is slowed down in comparison with low-molecular NLCs, which can cause an increase in the nonlinear optical response. Second, specific features of the reorientation dynamics associated with the complex nature of macromolecule rotation can manifest themselves.

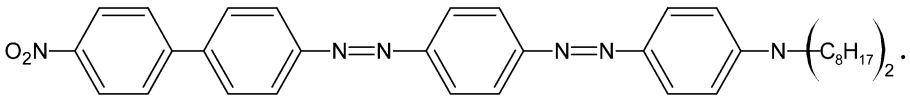
Optical reorientation of the director in the light-absorbing NLCP was first detected in [11]. In the present paper, we report on the first observation of optical orientation in transparent NLCP and the light-induced orientational phase transition in NLCP doped with dye.

Experimental samples and technique. The study was performed with a planar-oriented sample of polyacrylate (PAA)



(PAA)

and with a planar-oriented PAA sample doped with KD-1 diazobenzene dye (0.05% wt)



(KD-1)

The preparation technique of planar-oriented samples is described in [11]. The sample thickness was $L = 50$ μm. PAA polymer forms a nematic phase with an isotropization temperature of 123 °C; the glass-transition temperature is 26 °C. The degree of polymerization is 82, the polydispersity is ∼1.2. At room temperature, the wavelength of the absorption spectrum maximum for the PAA + 0.05% KD-1 sample, measured using an MS-122 spectrometer, was $\lambda = 512$ nm. The absorbances of extraordinary and ordinary waves at the wavelength $\lambda = 473$ nm are $n_e = 173$ cm^{-1} and $n_o = 29$ cm^{-1}.

The optical scheme of the experiment was similar to that used in [11]. The light beam of a solid-state laser with wavelength $\lambda = 473$ nm or $\lambda = 532$ nm was focused by a lens to NLCP. The waist radius for $\lambda = 473$ nm was $w_0 = 25$ μm. The experimental samples were placed so that the direction of the unperturbed director and the polarization direction were in the horizontal plane. The sample could be rotated about the vertical axis; in this case, the angle α of light incidence on the crystal was varied. In this geometry, the extraordinary light wave was excited in the crystal. The light beam passed through the NLCP was observed on the screen placed at a distance of ∼1 m behind the sample. The light beam power was measured using a Sanwa Electric LP1 device.

The optical orientation was studied using the self-action effect, i.e., self-focusing or self-defocusing of a light beam, caused by a change in the refractive index of the extraordinary wave due to the light-induced director rotation. At the large nonlinear phase shift $\Delta S = 2\pi|\Delta n|L/\lambda$ (Δn is the light-induced refractive index), the light beam self-action results in the formation of aberration rings [12], the number of which $N = \Delta S/2\pi$ makes it possible to determine the light-induced refractive index magnitude

$$|\Delta n| = \frac{N\lambda\cos\beta}{L},$$

where β is the light refraction angle in NLCP, related by Snell's law to the incidence angle α. The sense of the director rotation can be determined by the aberration pattern transformation during the crystal displacement perpendicular to the light beam [13].

Interaction of light with transparent nematic liquid crystalline polymer. The sample of polymer PAA was exposed to an obliquely incident ($\alpha = 40°$) light beam with $\lambda = 532$ nm and power $P = 60$ mW. For the time of ∼25 min, the pattern of two aberration rings was formed on the screen (Fig. 1(a)); in this case, the light polarization direction (horizontal) was retained. A small upward displacement of the cell with respect to the light beam resulted in disappearance of the lower aberration pattern area and additional illumination of the upper area (Fig. 1(b)). Such an intensity transformation of the aberration pattern corresponds to light beam self-focusing, i.e., a light-induced increase in the refractive index of the extraordinary wave and, hence, a director rotation parallel to the light field. The light-induced refractive index was $\Delta n \sim 0.02$. In order of magnitude, this value corresponds to a light-induced refractive index change in low-molecular liquid crystals.

The characteristic relaxation time determined using a probe beam is 20 min. This time is larger than the characteristic value for low-molecular nematic liquid crystals by two orders of magnitude.

Interaction of light with nematic liquid crystalline polymer doped with dye. During both the normal and oblique incidence of the light beam on the planar-oriented NLCP + 0.05% KD-1 sample, self-defocusing was observed, i.e., the NLCP director is rotated perpendicular to the light field; hence, the refractive index of the extraordinary wave decreased. The dependences of the magnitude of the stationary refractive index change, calculated by the number of aberration rings using Eq. (1), on the light beam power are shown in Fig. 2.

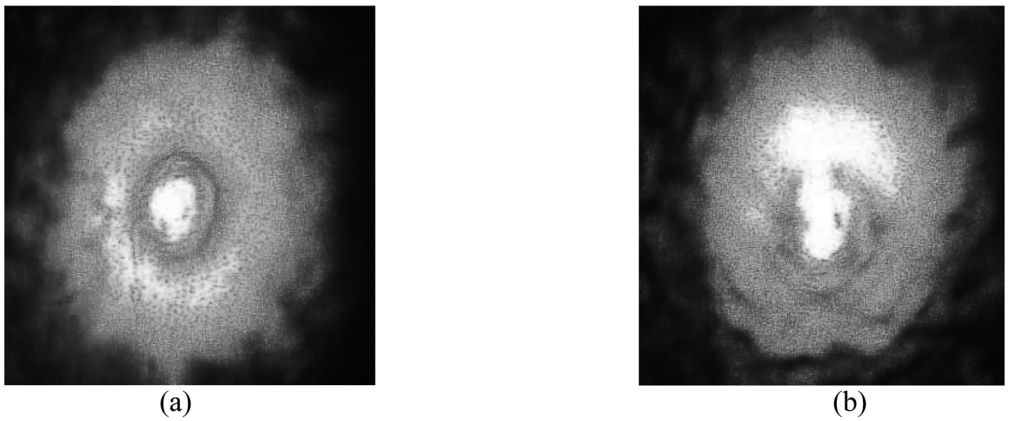


Fig. 1. Photographs of self-focusing aberration rings for the planar-oriented PAA sample 50 μm thick exposed to an obliquely ($\alpha = 40°$) incident light beam ($P = 60$ mW, $\lambda = 532$ nm): (a) stationary pattern and (b) nonstationary pattern after upward displacement of the crystal. Angular size of photographs is ~0.05 rad.

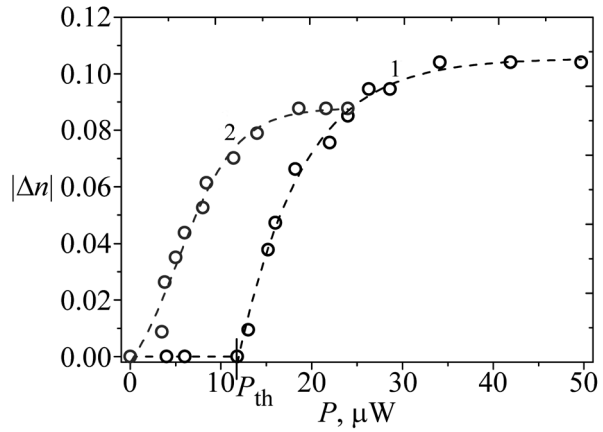


Fig. 2. Dependence of the stationary magnitude of the light-induced refractive index $|\Delta n|$ on the power P at (1) normal and (2) oblique light beam incidence ($\alpha = 40°$, $\lambda = 473$ nm) on PAA + 0.05% KD-1 nematic polymer; the sample temperature is $T = 110$ °C.

At the normal light incidence on dye-doped NLCPO, the dependence of the light-induced refractive index on the beam power corresponds to the threshold director reorientation (Fig. 2, curve 1). The threshold power is $P_{\rm th} = 12$ μW (the power density on the beam axis $I = 2P/\pi w_0^2$ is 0.3 W/cm^2). At the power $P \sim 3P_{\rm th}$, the light-induced refractive index reaches saturation corresponding to the maximum director rotation by 90°. At the oblique incidence, reorientation is nonthreshold.

Thus, the experimental results obtained suggest that the light-induced threshold orientation transition occurs in NLCPs, which is similar to the effects characteristic of low-molecular nematics.

The characteristic time of threshold reorientation at $P \sim P_{\rm th}$ is ~1 hour; in the case of a tenfold excess of the threshold power, this value is ~10 min. The characteristic relaxation time is 12 min.

The measured threshold power $P_{\rm th} = 12$ μW is lower than the threshold of the light-induced Freedericksz transition in low-molecular transparent nematics by four orders of magnitude [4] and is lower than the characteristic value for low-molecular nematics with an azobenzene polymer impurity by two orders of magnitude [13]. The nonlinearity coefficient $n_2 = |\Delta n|/I$ during the threshold transition in NLCPs is ~0.1 cm^2/W ($|\Delta n| = 0.1$ at $P = 3P_{\rm th}$). This value is two hundred times larger than the corresponding value for low-molecular NLC with dye dopants. Such a significant increase in the nonlinearity coefficient is caused by an increase in the rotational diffusion time of azo dye.

Conclusions. Optical orientation in transparent nematic liquid crystalline polymer (NLCP) was observed for the first time. In NLCP with dye dopant, the second-order light-induced orientation transition was found, which is an analogue of the Freedericksz transition in low-frequency fields.

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