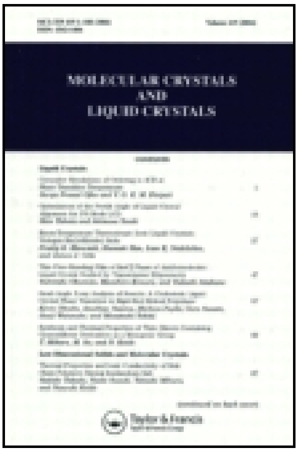

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Light Interaction with NLCs Doped with Comb-Shaped Azopolymers with Different Degrees of Polymerization

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Light Interaction with NLCs Doped with Comb-Shaped Azopolymers with Different Degrees of Polymerization

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The light-induced director reorientation in NLCs doped with the comb-shaped azopolymers with different degrees of polymerization (the number of chromophore groups) has been studied. The negative optical nonlinearity (a decrease in the refractive index of the extraordinary wave due to the director rotation away from the light field) was observed for all dopants. It was found that the threshold power of the Freedericksz transition decreases with the polymerization degree. The light-induced Freedericksz transition of the first order was observed for the dopants with lower degrees of polymerization.

Keywords: Nematic liquid crystals; azodopants; comb-shaped polymers; first-order Freedericksz transition

1. Introduction

It is well known that various dyes can induce orientational optical nonlinearity in a nematic host [1–6]. The reason for this nonlinearity is the director reorientation under action of the torque produced by changing the intermolecular forces under dye excitation [1, 5, 7]. This torque can be written in the form

$$\mathbf{\Gamma} = \frac{\Delta\varepsilon_{\text{eff}}}{8\pi}(\mathbf{nE})[\mathbf{n} \times \mathbf{E}], \qquad (1)$$

where $\Delta\varepsilon_{\text{eff}}$ is the effective optical anisotropy, which is the product of the actual optical anisotropy $\Delta\varepsilon$ and the enhancement factor η [1].

Large negative nonlinearities (a decrease in the refractive index of the extraordinary wave due to the light-induced director rotation away from the light field ($\Delta\varepsilon_{\text{eff}} < 0$)) are produced by high-molar-mass compounds of different architecture – comb-shaped

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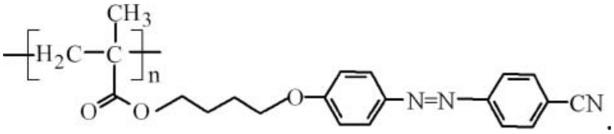
polymers and dendrimers [5, 8–11]. The nonlinearity induced by low-molar-mass dyes similar in structure to the chromophores of the polymers is lower in magnitude than that induced by the polymers. In addition, the nonlinearity related to the low-molar-mass dyes is sign-variable: at a certain angle Ψ between the light field **E** and the NLC director **n** the negative nonlinearity is replaced by the positive one (in which case the refractive index increases due to director rotation to the light field). The detailed studies of light interaction with NLCs doped with the dendrimers of different generations [9, 10] showed that the nonlinearity increases in magnitude with the generation number and is negative (except for the dendrimer of the first generation, in which case it is sign-variable). For the second and third dendrimer generations, the light induced Freedericksz transition (occurred at the normal light incidence on planar cells) of the first order and the optical bistability were observed for the first time in the linearly polarized light wave in the absence of additional fields [10, 12, 13]. The reasons for the influence of the molecular structure of the dyes on the induced nonlinearity are not clear yet; their elucidation requires further experimental and theoretical studies.

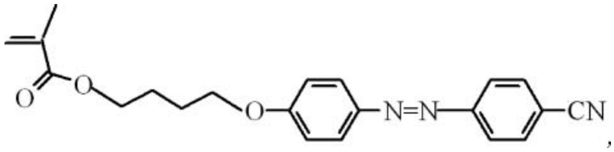
The objective of this paper is to investigate the influence of the degree of polymerization of the comb-shaped azopolymers, used as dopants, on the light interaction with NLCs.

2. Experimental

The investigation was carried out on the host ZhKM-1277 (NIOPIK, Russia) exhibiting the nematic phase in the wide temperature range from - 20°C to 60°C. The refractive indices of this material at room temperature are 1.71 and 1.52 (at $\lambda = 589$ nm). The dopants were the comb-shaped azopolymers denoted as Pn, their chemical structure is shown below:



Here n (n = 14, 29, 43, 97) is the degree of polymerization (corresponds to the number of light-absorbing side azobenzene groups attached to alkyl chain). The weight-average molecular weight is $M_w = 5.1 \cdot 10^3$ (P14), $10.4 \cdot 10^3$ (P29), $14.6 \cdot 10^3$ (P43), $35.2 \cdot 10^3$ (P97). We also studied the mixture of ZhKM-1277 and the low-molar-mass dye D



similar in structure to the polymer side-chain azofragment. The concentration of all dopants was 0.5 wt%. The cells had homeotropic and planar alignment; the cell thickness was L = 100 μm.

Liquid crystal mixtures absorb light in the blue-green spectral range. Absorption coefficients for the extraordinary and ordinary waves (at $\lambda = 473$ nm) are $\alpha_{\|} = 78$ (D), 102 (P14), 90 (P29), 83 (P43), 79 (P97) cm^{-1} and $\alpha_{\perp} = 21$ (D), 31 (P14), 27 (P29), 22 (P43), 24 (P97) cm^{-1}.

Light interaction with NLCs was investigated using the self-phase modulation technique [8, 14]. This method is based on the registration of the number N of aberrational rings in the cross section of the light beam passed through an NLC cell. The value of refractive index variation |Δn| is related to N by the formula

$$|\Delta n| = N\lambda\cos\beta/L, \tag{2}$$

where β is the angle of refraction. The orientational and thermal mechanisms of the NLC-light interaction can be distinguished by the dynamics of the aberration pattern formation (the characteristic times for the orientational and thermal nonlinearities in the cell with the thickness $L \sim 100\ \mu m$ are ~10 s and $\sim 10^{-2}$ s, respectively). The sign of Δn (or the nonlinearity sign) is determined from the ring intensity redistribution upon rapid shift of the NLC cell perpendicularly to the light beam.

In experiment, the p-polarized light beam from a cw solid-state laser ($\lambda = 473$ nm) was focused by a lens with $f = 18$ cm into the NLC cell. The unperturbed NLC director was in the horizontal plane. The angle of incidence α was changed by rotating the cell about the vertical axis. The aberration rings were observed on a screen behind the cell.

3. Results and Discussion

The light interaction with all samples was of orientational origin (the contribution of the thermal nonlinearity was small).

The orientational nonlinearity induced by dye D was sign-variable (negative for the homeotropic cell and positive for the planar one). The number of aberration rings was rather small ($N < 6$). The sign-variable type of orientational nonlinearity is characteristic of most low-molar-mass azodyes [3, 14–16]. The dependence of the sign of the nonlinearity (and $\Delta\varepsilon_{\text{eff}}$) on the angle Ψ is explained in [15] by the influence of the light field on the conformational composition of the azodye molecules. Due to the difference in the order

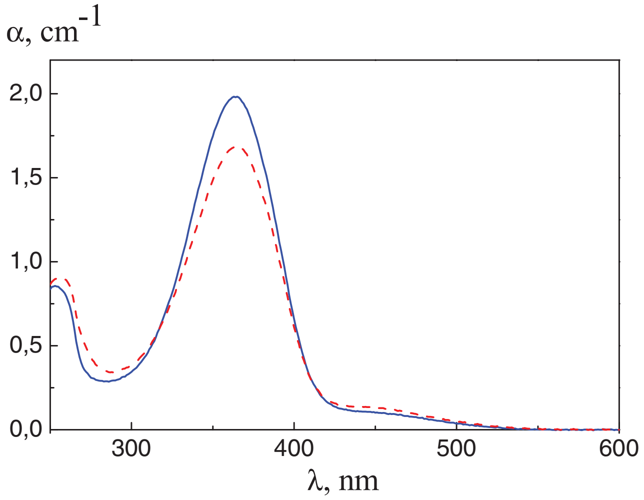


Figure 1. Absorption spectra of dye D dissolved in dichloroethane (dye concentration is $1.12\cdot10^{-2}$ mg per milliliter) before (solid line) and after (dashed line) light illumination ($\lambda = 473$ nm, power density $\sim 3\cdot10^{-2}$ W/cm^2, exposure time 5 min).

parameters of the cis- and trans-isomers, this composition depends on Ψ, which leads to the corresponding change in the nonlinearity (since the cis- and trans-isomers induce the positive and negative nonlinearities, respectively). For dye D, the photoconformational activity was confirmed by the measurement of the absorption spectrum of the dye solution in dichloroethane under laser illumination (Fig. 1). However, detailed analysis of the sign-variable nonlinearity requires spectral measurements in nematic phase, which are hindered by the host molecule absorption.

The optical nonlinearity induced by all polymeric dopants was negative for both homeotropic (Fig. 2a) and planar (Fig. 2b) cells. The number N of the self-defocusing aberration rings for oblique ($\alpha = 40°$) light incidence first increases monotonously with the light beam power P and then saturates. Figure 2 also shows the calculated (using relation (2)) power dependences of the magnitude of the light induced refractive indices. It

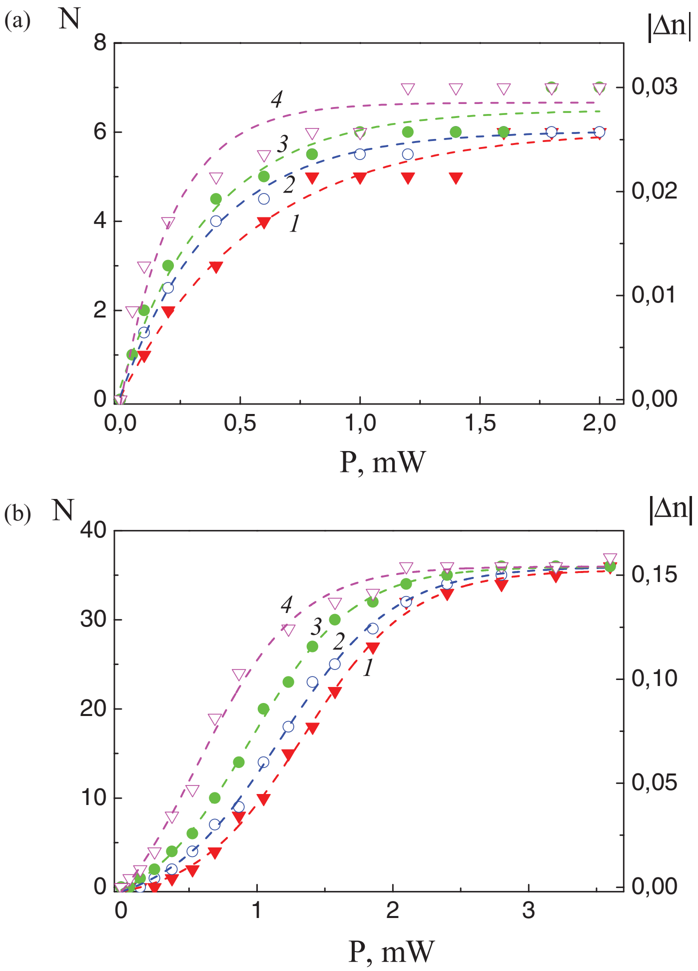


Figure 2. Dependences of the number N of the self-defocusing aberration rings and the magnitude of the averaged light-induced refractive index |Δn| for the light beam ($\lambda = 473$ nm, $\alpha = 40°$) passed through (a) homeotropic and (b) planar NLCs ZhKM-1277 doped with the polymers (*1*) P14, (*2*) P29, (*3*) P43, and (*4*) P97 on the light beam power P.

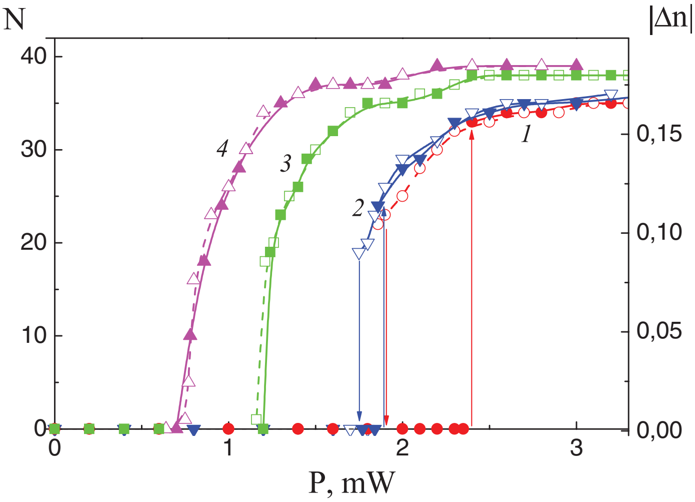


Figure 3. Dependences of the number N of the self-defocusing aberration rings and the magnitude of the averaged light-induced refractive index |Δn| for a light beam ($\lambda = 473$ nm, $\alpha = 0°$) passed through planar NLCs ZhKM-1277 doped with the (*1*) P14, (*2*) P29, (*3*) P43, and (*4*) P97 polymers on the light beam power P. Solid symbols correspond to increasing P; open symbols, to decreasing P.

can be seen from Fig. 2 that the optical response increases with the degree of the dopant polymerization.

Dependences N(P) and |Δn(P)| obtained for the normal light incidence on the planar cells are shown in Fig. 3. In this case, we observed the threshold director reorientation, characteristic of the Freedericksz transition.

For n = 14 and 29 the transition is first order. Thus, for n = 14, an abrupt increase in the ring number from N = 0 to N = 32 occurs at $P_{1th} = 2.4$ mW. At subsequent decrease in P, the aberration pattern exists to $P_{2th} = 1.85$ mW, at which power it collapses (N changes from 23 to 0). The relative width of the bistability region is $\Delta = (P_{1th}\text{-}P_{2th})/P_{1th} = 0.23$. For n = 43 and 97 the number N changes continuously; that is, the Freedericksz transition is of the second order. The threshold of the Freedericksz transition decreases with the degree of the polymerization from 2.4 mW at n = 14 to 0.7 mW at n = 97.

Comparing the data obtained with those reported in [10], we can see the coincidence of the main regularities manifested at increasing the degree of polymerization n of the comb-shaped polymers and the generation number G of the dendrimers: (1) an increase in the optical response and (2) occurrence of the first-order Freedericksz transition at smaller n and G.

The optical response induced by dyes can be characterized by the ratio $\eta_\alpha = \Delta\varepsilon_{\text{eff}}/(\alpha_{\|}+2\alpha_{\perp})$. To estimate this ratio at $\Psi = 0$, we notice that $P_{\text{th}} \sim 1/\Delta\varepsilon_{\text{eff}}$. Then $\eta_\alpha \sim 1/(\alpha_{\|}+2\alpha_{\perp})P_{\text{th}}$. The dependence of the quantity $\eta\prime = (\alpha_{||}+2\alpha_{\perp})^{-1}P_{\text{th}}^{-1}$on the degree of polymerization is shown in Fig. 4. It can be seen from Fig. 4 that the polymer-induced optical response of the composite liquid-crystalline system increases with the degree of polymerization n almost linearly. It should be noted that in above consideration we neglected the torque acting on the nematic matrix (on the light-induced dipoles), because the typical threshold of the Freedericksz transition in a pure (undoped) host is of the order of 100 mW, i.e., much higher than the threshold in the composite systems under study.

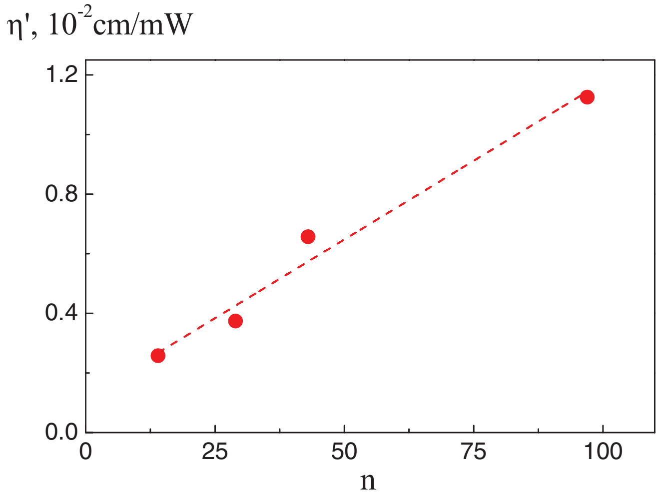


Figure 4. Dependence of the parameter $\eta' = (\alpha_{||}+2\alpha_{\perp})^{-1}P_{th}^{-1}$on the dopant polymerization degree n. Dashed line is the linear fitting.

The occurrence of the first-order Freedericksz transition in the dendrimer–NLC system was explained [13] by the feedback between the director rotation and the torque (1) due to the angular dependence of the effective optical anisotropy $\Delta\varepsilon_{\mathrm{eff}}(\Psi)$. This dependence was taken in the form

$$\Delta\varepsilon_{\mathrm{eff}} = \Delta\varepsilon^{(0)}(1 + \mathrm{m}\sin^2\Psi), \tag{3}$$

where $\Delta\varepsilon^{(0)} = \Delta\varepsilon_{\mathrm{eff}}(\Psi = 0)$. The parameter m is related to the bistability region width. For $\Delta = 0.23$ ($n = 14$), we obtained $m = 2.1$. The corresponding angular dependence of the effective optical anisotropy is illustrated in Fig. 5. Disappearance of the bistability and changing the Freedericksz transition order with increasing the polymerization degree n corresponds to a decrease in the parameter m.

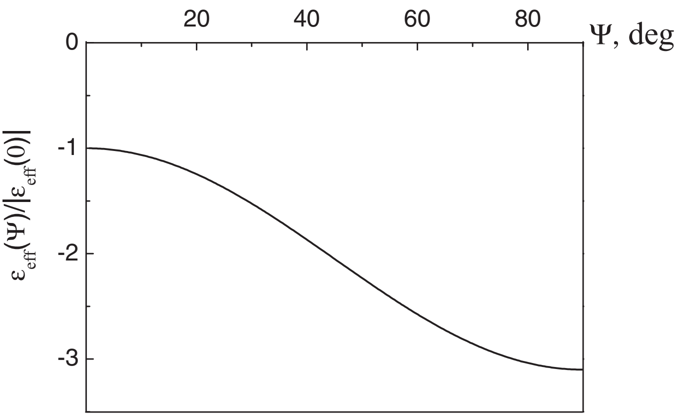


Figure 5. Dependence of the ratio $\Delta\varepsilon_{\mathrm{eff}}(\Psi)/|\Delta\varepsilon_{\mathrm{eff}}(\Psi = 0)|$ on the angle Ψ between the light field **E** and NLC director **n** calculated for the NLC ZhKM-1277 doped with the P14 polymer.

The existence of angular dependence of the effective anisotropy can, in principle, be explained, as in the case of the low-molar-mass dye D, by the photoconformational transitions. Our measurements for the polymer P97 dissolved in dichloroethane showed almost the same change in the absorption spectrum, related to the photoconformational transitions, as for dye D.

The explanation of the dependence of the nonlinear optical response on the degree of the polymerization requires additional information, including the data on the molecular ordering of the polymers in nematic host, the influence of the nematic host on the trans-cis isomerization, and the rotational diffusion.

4. Conclusions

The light-induced director reorientation in NLCs doped with the comb-shaped azopolymers with different degrees of polymerization n = 14, 29, 43, 97 has been studied. The negative optical nonlinearity was observed for these dopants. It was found that the threshold power of the Freedericksz transition decreases with the polymerization degree. The light-induced Freedericksz transition of the first order was observed for the dopants with n = 14, 29. Main regularities manifested at increasing the degree of polymerization n of the comb-shaped polymers are the same as those previously reported for the azodendrimers with different generation number, which suggests the similarity of the mechanisms responsible for modification of the nonlinear optical response with increasing the molecular weight.

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