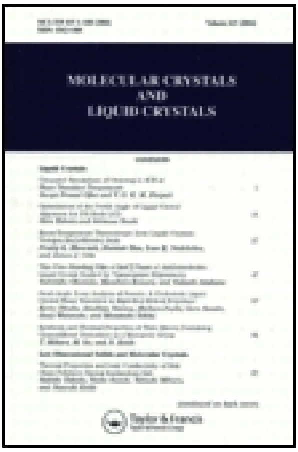

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Optical Director Reorientation in NLCs Doped with Light-Absorbing Codendrimers of Different Generations

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The orientational optical nonlinearity induced in NLCs by light-absorbing carbosilane codendrimers with statistical distribution of terminal aliphatic and azobenzene fragments has been studied comparatively for different (from the second to the fourth) codendrimer generations. It was found that all the codendrimers induce the negative nonlinearity (director rotates away from the light field thus decreasing the refractive index of the extraordinary wave). The orientational response increases with the generation number. The optical bistability is manifested for NLCs doped with the codendrimers of the second and third generations.

Keywords Dendrimers; light-induced Freedericksz transition; nematic liquid crystals; orientational nonlinearity

1. Introduction

The optical axis of nematic liquid crystals (NLCs) can be easily rotated by external influences, e.g., the light field [1–10]. Director rotation in pure (undoped) nematics occurs toward the light field and is due to force action on light-induced dipoles. The corresponding orientational optical nonlinearity is nine orders of magnitude larger than the Kerr nonlinearity of ordinary liquids [1,4].

Doping of the nematic host with low-molar-mass dyes can significantly increase the orientational response of liquid crystal system (by two orders of magnitude at the dye concentration less than 1 wt% [5–10]). In dye-doped NLCs, the director can be rotated not only toward the light field but also perpendicular to it [6]. In the latter case, the refractive index of the extraordinary wave decreases and, correspondingly, an NLC exhibits a negative orientational nonlinearity. A specific phenomenon was

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observed for NLCs doped with azodyes [7]: the nonlinearity sign of the dye-doped NLC depended on the angle between the director and the light field (sign-inversion nonlinearity). The mechanism of the dye-enhanced optical director reorientation is related to changing intermolecular forces under dye excitation.

High-molar-mass dopants are also attractive for inducing director reorientation in NLCs. It was found previously, that comb-shaped polymers induce orientational nonlinearity greater than that in the case of low-molar-mass azodyes similar in structure to photochromic groups of the polymers [9]. The nonlinearity sign of the polymer-doped NLC was negative, while the NLC doped with the azodye exhibited the sign-inversion nonlinearity.

Similar nonlinearity behavior was observed for the homodendrimer of the fifth generation and the azodye identical to dendrimer terminal fragments [11,12]. In [12], it was also found that the homodendrimer of the first generation induces sign-inversion nonlinearity. In [13], the light interaction with planar NLC doped with the second-generation carbosilane dendrimer with statistically distributed terminal aliphatic and azobenzene groups was studied. The orientational optical nonlinearity was found to be negative and the director field bistability was observed.

Below, we present the detailed comparative study of the orientational nonlinearity induced in NLCs by the carbosilane codendrimers of different (from the second to the fourth) generations.

2. Experimental

The study was performed with homeotropic and planar samples of nematic host ZhKM-1277 doped with carbosilane dendrimers. The dopant concentration was 0.15 wt%. The ZhKM-1277 material exhibits the nematic phase in the temperature range from $-20°C$ to $60°C$ and has a positive dielectric anisotropy. Its refractive indices are $n_{\|} = 1.71$ and $n_{\perp} = 1.52$ at $\lambda = 589$ nm. The thickness of liquid crystal cells was 100 μm.

The dendrimers (Fig. 1) contain terminal aliphatic and mesogenic azobenzene fragments, which were statistically distributed over the dendritic surface. Dendrimers synthesis and properties are described in [14].

The absorption of the NLC cell was measured by an MS-122 spectrophotometer (PROSCAN Special Instruments). The data obtained indicate a sufficiently large dichroism of the dendrimer–NLC systems. For instance, in the case of the G4-doped NLC the absorption coefficients at the wavelength $\lambda = 473$ nm for the extraordinary and ordinary waves are $\alpha_{\|} = 20.1\,\text{cm}^{-1}$ and $\alpha_{\perp} = 10.4\,\text{cm}^{-1}$, respectively.

We used the technique of aberrational self-phase modulation of the light beam [11,15]. The light source was a cw solid-state laser LCS-DTL-364 ($\lambda = 473$ nm). Linear polarization of the light beam could be rotated by a double Fresnel rhomb. The plane of liquid crystal layer was vertical; unperturbed NLC director was in the horizontal plane. The NLC cell could be rotated about the vertical axis to change the incidence angle α. The system of aberration rings was observed on the screen placed behind the cell.

The number N of the aberration rings is connected with the nonlinear phase shift ΔS_{NL} for the extraordinary wave as

$$N = |\Delta S_{NL}|/2\pi.$$

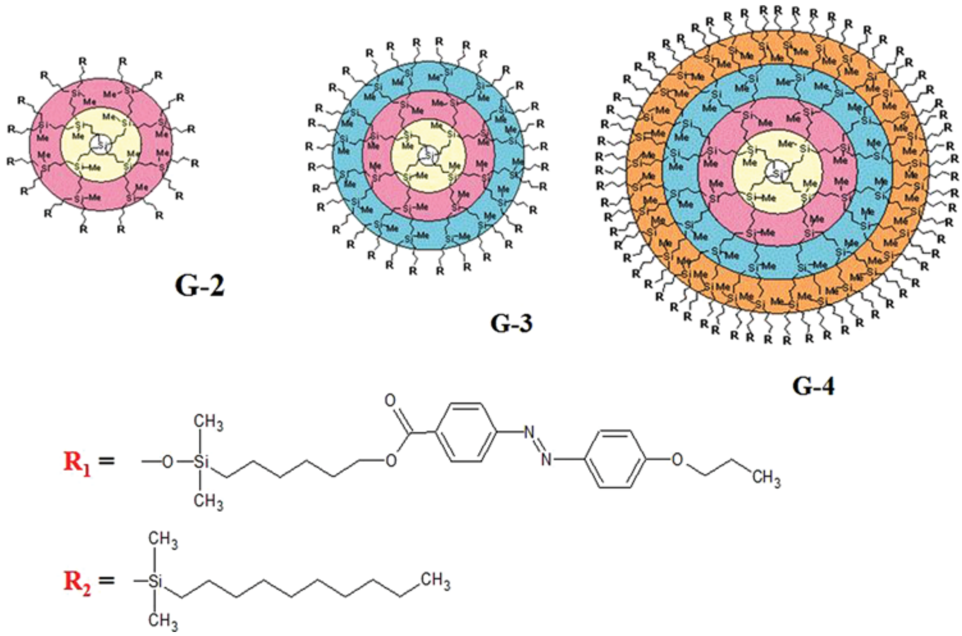

Figure 1. Carbosilane codendrimers of the second, third, and fourth generations. (Figure appears in color online.)

The phase shift ΔS_{NL} is expressed in terms of the change in the refractive index Δn for extraordinary wave averaged over the cell thickness

$$\Delta S_{NL} = 2\pi \Delta n L/\lambda,$$

where L is the cell thickness and λ is the wavelength. The sign of the light-induced refractive index (that is, the sense of the director rotation) was determined by the intensity redistribution in the aberration pattern at the rapid shift of the NLC cell upward relative to incident beam.

3. Results and Discussion

Illumination of all samples with the p-polarized light beam results in appearance of the aberration pattern of orientational nature, which was evidenced by the characteristic times of the pattern formation at oblique incidence and relaxation ($\sim$10 s).

For all samples and experimental geometries, we only observed the self-defocusing of the light beam, which implies that director rotates away from the light field (i.e. the nonlinearity is negative). Negative nonlinearity proves that the director reorientation is due to the presence of dendrimers, because the nonlinearity of undoped nematic host is always positive.

Dependences of the number N of the self-defocusing aberration rings and the magnitude of the averaged light-induced refractive index $|\Delta n|$ for a light beam obliquely incident on planar and homeotropic cells on the beam power P are shown in Figure 2. It is clearly seen that orientational response of liquid crystal system increases with the dendrimer generation number.

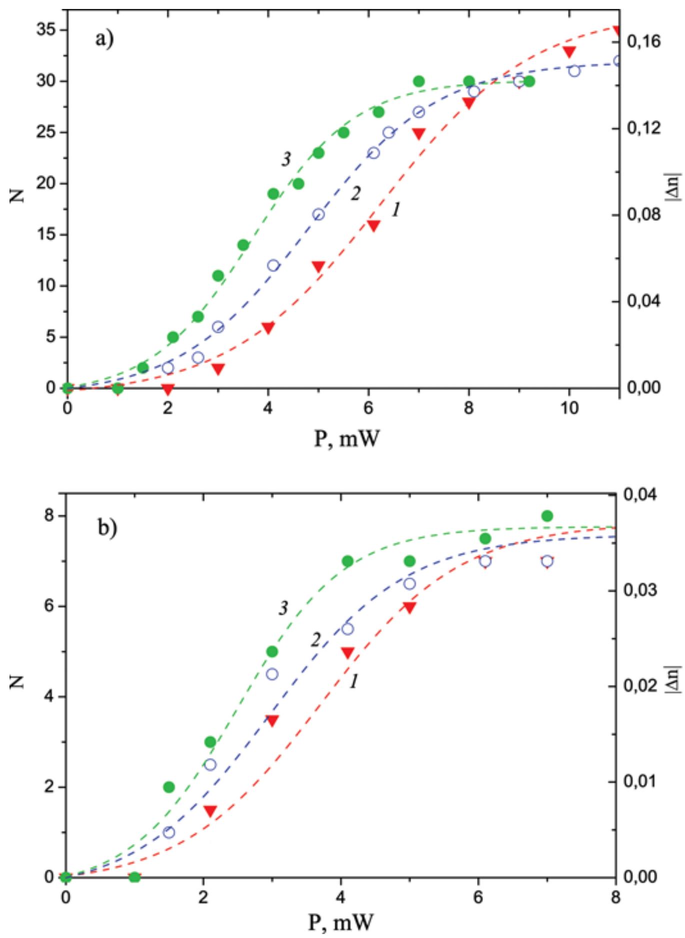

Figure 2. Dependences of the number N of the self-defocusing aberration rings and the magnitude of the averaged light-induced refractive index Δn for the light beam ($\lambda = 473\,\mathrm{nm}$, $\alpha = 50°$) passed through (a) planar and (b) homeotropic NLCs doped with the dendrimers (*1*) G2, (*2*) G3, and (*3*) G4 on the light beam power P. (Figure appears in color online.)

We estimated the enhancement of the nonlinear optical response for planar NLC doped with G4 dendrimer. To this end, we determined the ratio of the light-beam powers at which an equal number of rings was observed for the homeotropic cell with pure host and the planar cell with the doped host and then divided it by the quantity $\alpha' = \alpha_{\|} + 2\alpha_{\perp}$ (which is proportional to the NLC absorptivity averaged over the director orientation). The calculated parameter $\eta_\alpha = -0.42\,\mathrm{cm}$ (the minus sign indicates the negative nonlinearity) is smaller in magnitude than the parameter $\eta_\alpha = -2.3\,\mathrm{cm}$ obtained for nematic host doped with comb-like polymer [9] and the value $\eta_\alpha = -0.94\,\mathrm{cm}$ obtained for the homodendrimer of the fifth generation G5 (containing another azochromophore) [12].

Dependences of the aberration ring number and the magnitude of the light-induced refractive index on the direction of light-beam polarization are shown in Figure 3. It can be seen from this figure that polarization rotation from the p-polarization ($\varphi = 0°$) to the s-polarization ($\varphi = 90°$) leads to monotonic

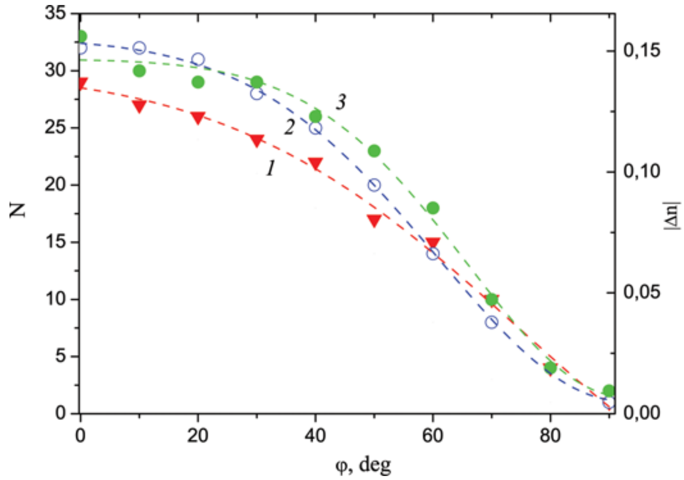

Figure 3. Dependences of the number N of the self-defocusing aberration rings and the magnitude of the averaged light-induced refractive index Δn on the angle φ of the light field polarization rotation ($\lambda = 473\,\mathrm{nm}$, P = 8 mW, $\alpha = 50°$) for planar NLCs doped with 0.15 wt% of (*1*) G2, (*2*) G3, and (*3*) G4 dendrimers. Angle $\varphi = 0°$ corresponds to the extraordinary wave; $\varphi = 90°$, to the ordinary wave. (Figure appears in color online.)

suppression of the aberration pattern. Such behavior is characteristic of orientational nonlinearity in nematics and indicates the absence of significant thermal effects.

Application of external low-frequency voltage ($\nu = 3\,\mathrm{kHz}$) to homeotropic samples results in suppression of aberration rings due to elimination of light-induced director field inhomogeneity and reversion of NLC to the initial state. In the case of planar samples, the dependence is nonmonotonic (see Fig. 4 for the G3-doped

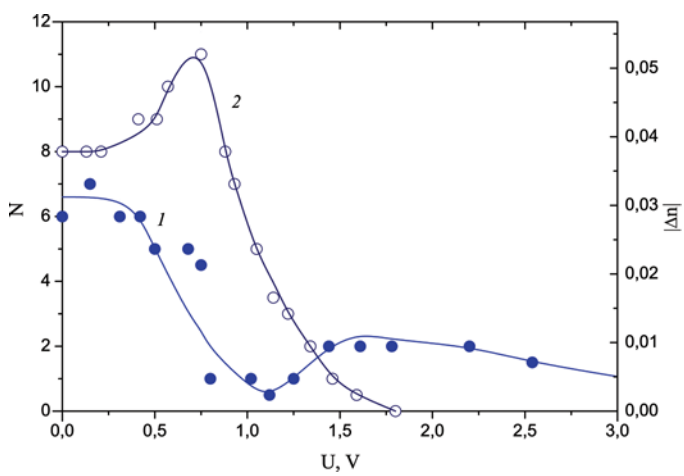

Figure 4. Dependences of the number N of the self-defocusing aberration rings and the magnitude of the averaged light-induced refractive index Δn on the applied low-frequency ($\nu = 3\,\mathrm{kHz}$) voltage U at illumination ($\lambda = 473\,\mathrm{nm}$, P = 3 mW) of planar ZhKM-1277 + 0.15% G3. Curve *1* corresponds to $\alpha = -50°$; curve *2*, to $\alpha = +50°$. (Figure appears in color online.)

sample) and is affected by the sense of the NLC cell rotation (the sign of the incidence α). These features can be explained by the complex character of the ac field influence on the optical nonlinearity (the low field enhances the nonlinearity, while the high field suppresses it) and the surface pretilt [12].

The observed variation in the nonlinearity with the dendrimer generation number may be due to changing the dendrimer photoisomerization properties [11]. The trans-isomers of low-molar mass azobenzene molecules induce negative nonlinearity in the NLC, whereas the cis-isomers induce positive nonlinearity [16]. Under exposure to light, the isomers are excited and can undergo the conformational transitions. We can assume that the equilibrium concentration of cis isomers of the dendrimer chromophores and their angular distribution in the light field varies with the dendrimer generation number.

At normal light incidence on planar samples the director reorientation exhibits the threshold behavior, which is a characteristic feature of the Freedericksz transition in NLC (Fig. 5). As follows from the figure, the Freedericksz threshold power decreases (i.e., the optical response increases) with the dopant generation number. It is also seen that Freedericksz transitions for the second and the third generations are accompanied by the director field bistability. The width of the bistability region decreases with the dendrimer generation number (from G2 to G3); for the G4 dendrimer no bistability was observed. The appearance of the bistability can be due to the dependence of the enhancement factor of the light-induced torque (with respect to the undoped nematic host) on the angle between the light field **E** and director **n**. The detailed study of the bistability phenomena will be presented elsewhere.

4. Conclusions

The light-induced molecular reorientation in NLCs doped with the codendrimers of various (2–4) generations was experimentally studied. It was found that for all the

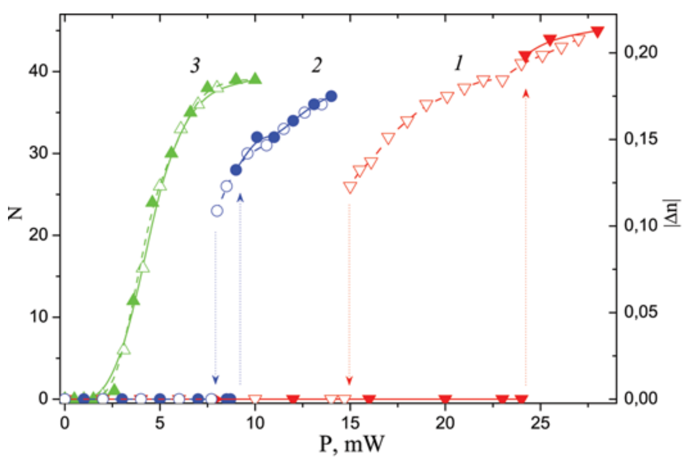

Figure 5. Dependences of the number N of the self-defocusing aberration rings and the magnitude of the averaged light-induced refractive index Δn for a light beam ($\lambda = 473$ nm, $\alpha = 0°$) passed through planar NLC ZhKM-1277 doped with the (*1*) G2, (*2*) G3, and (*3*) G4 dendrimers on the light beam power P. Solid symbols correspond to increasing P; open symbols, to decreasing P. (Figure appears in color online.)

dopants the NLC director rotates away from the light field irrespective of the experimental geometry, i.e., the direction of the light propagation (relative to the director) and the light polarization. The complication of dendrimer structure (generation number) enhances the orientational optical response of the liquid crystal system. In particular, the light-induced Freedericksz transition threshold decreases by a factor of about 10 when passing from the second to the fourth generation. The width of bistability region (manifested at normal light incidence) decreases with the dendrimer generation number.

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