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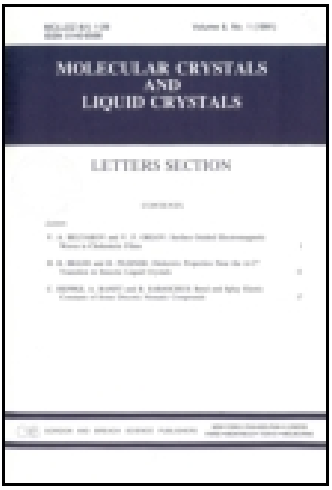

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Distribution of Dye and Mesogen Molecules Orientation in Photoaligning Layer vs. Aperture of Polarized Light Beam

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Distribution of Dye and Mesogen Molecules Orientation in Photoaligning Layer vs. Aperture of Polarized Light Beam

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Orientation of dyes and liquid crystals molecules in the field of laser radiation is considered taking into account anisotropy of molecular optical polarizability. A dependence of dyes and liquid crystals clusters energy on the strength of laser radiation electrical field, aperture of the light beam, optical polarizability anisotropy, order parameter and the number of molecules in a cluster, is derived. The angular distribution function of clusters is derived depending on the aperture of the light beam.

Keywords Dyes; liquid crystals; photoalignment; laser irradiation; polarized light; aperture

Photoalignment of liquid crystals (LC) and dyes [1–7] is one of modern methods used in LC TV sets, LC monitors and other optical LC-based devices. Using of directed laser radiation allows fabrication of photoaligning films with enhanced structure and properties. A theory of this phenomenon [8] is based on a solution of a diffusion equation. It provided calculation of the material order parameter *vs.* time. However a dependence of the molecules angular distribution as a function of the recording light beam direction and aperture has not been considered.

The aim of the presented paper is to find the angular distribution of the LC or dye director in a cluster oriented by the polarized laser beam and its dependence on the LC and dyes properties as well as laser radiation angular parameters.

Energy of interaction of the electric field with a molecule is defined by equation as follows:

$$U = -\tfrac{1}{2}\sum_{i,j}\alpha_{ij}E_iE_j,$$

$i, j = x, y, z; \alpha_{ij}$ – components of the polarizability tensor of the molecule; E_i, E_j – components of the electric field vector in the same coordinate system.

Let a ray with wave vector $\vec{k}$ is incident under angle γ in relation to the photoaligning film's normal $\vec{n}$. The plane $y0z$ is radiation polarization plane (Fig. 1).

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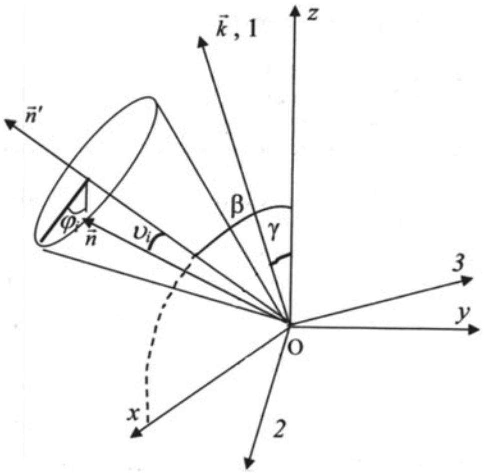

Figure 1. Orientation of the dye or mesogen molecule in relation to the laboratory coordinate system *xyz*. The *z* axis is perpendicular to the film boundary; *n* and $\vec{n}'$ are directions of the polarizability ellipsoid axis of the molecule and the cluster director, accordingly; $\vec{n}'$ lies in the *x*0*z* plane; υ_i and φ_i are polar and azimuthal angles that define the molecule orientation in the cluster coordinate system *x'y'z'* (*z'* axis is along $\vec{n}'$); $\vec{k}$ is the wave vector of the laser radiation; γ is the angle between the *z* axis and wave vector; β is the angle between the *z* axis and the cluster director.

The wave vector and electric field are directed along the axes 1 and 2, accordingly. The electric field strength components E_x and E_z are to find by using a matrix of transition from the coordinate system based on the wave vector to the laboratory coordinate system [8]

$$E_x = E_0 (\cos\phi \cdot \cos\psi \cdot \cos\gamma - \sin\phi \cdot \sin\psi),$$

$$E_y = E_0 (\cos\phi \cdot \sin\psi + \sin\phi \cdot \cos\psi \cdot \cos\gamma),$$

$$E_z = -E_0 \sin\gamma \cdot \cos\psi.$$

where γ is polar angle of the axis 1 in the fixed coordinate system; ϕ is the azimuth angle of the axis 1 (angle between planes *xz* and 1*z*); ψ is the azimuth angle of the fixed system (angle between planes 1*z* and 12). For $\gamma = 0\ \phi = \psi = 0$.

As the radiation is polarized $\vec{E}$ lies in the *x*0*z* plane, then $E_y = 0$ and $\cos\phi \cdot \sin\psi + \sin\phi \cdot \cos\psi \cdot \cos\gamma = 0$ и $tg\psi = -tg\phi \cdot \cos\gamma \Rightarrow \psi = -arctg\,(tg\phi \cdot \cos\gamma)$.

Therefore

$$E_x = E_0 \left\{ \cos\phi \cdot \cos\left[-arctg\left(tg\phi \cdot \cos\gamma\right)\right] \cdot \cos\gamma - \sin\phi \cdot \sin\left[-arctg\left(tg\phi \cdot \cos\gamma\right)\right] \right\}$$

$$E_y = 0,\ \ E_z = -E_0 \sin\gamma \cdot \cos\left[-arctg(tg\phi \cdot \cos\gamma)\right]$$

The components of the polarizability tensor of the molecule in the coordinate system x', y', z', related to the dye or LC cluster are defined by relation as follows:

$$\alpha_{ij} = \sum_{\sigma,\tau} \alpha_{\sigma\tau}(\sigma, i)(\tau, \mathrm{j})$$

where $i,\ j = x',\ y',\ z'; \sigma, \tau = 1, 2, 3; a_{\sigma\tau}$ and a_{ij} are components of the polarizability tensor in the coordinate systems related to the molecule and the cluster.

The polarizability ellipsoid of the molecule is considered as axially symmetric, $\alpha_{11} \equiv \alpha_1, \alpha_{22} = \alpha_{33} \equiv \alpha_2$. The transformation of the coordinate system related to the cluster to the laboratory coordinate system for the molecular polarizability components parallel and perpendicular to the cluster director $\vec{n}'(\alpha_{||}$и $\alpha_{\perp}$, accordingly) is described by the transition matrix. By using this matrix and equiprobable distribution of the molecules on angle ϕ_i one can obtain [9]:

$$\alpha_{||} = (\alpha_1 - \alpha_2)\cos^2\vartheta_i + \alpha_2,$$

$$\alpha_{\perp} = \tfrac{1}{2}(\alpha_1 - \alpha_2)\sin^2\vartheta_i + \alpha_2,$$

where $\vartheta_i$is the angle between directions of the molecule symmetry axis and director.

If make an averaging on ϑ_i and take into account $\overline{\cos^2\upsilon_i} = \frac{2S+1}{3}$ and $\overline{\sin^2\upsilon_i} = \frac{2-2S}{3}$, where S is the order parameter $S = \frac{3\overline{\cos^2\upsilon_i}-1}{2}$ one can obtain:

$$\alpha_{||} = \frac{2S+1}{3}(\alpha_1 - \alpha_2) + \alpha_2,\ \alpha_{\perp} = \frac{1-S}{3}(\alpha_1 - \alpha_2) + \alpha_2.$$

If the angle between the cluster director and the normal to the film surface (z axis) is equal to β, then the components the molecular polarizability tensor in the coordinate system related to the aligning film boundary are equal to:

$$\alpha_{xx} = (\alpha_1 - \alpha_2)\left(\tfrac{1-S}{3} + S\sin^2\beta\right) + \alpha_2,$$

$$\alpha_{xz} = \alpha_{zx} = (\alpha_1 - \alpha_2)\,S\sin\beta\cos\beta,$$

$$\alpha_{zz} = (\alpha_1 - \alpha_2)\left(\tfrac{1-S}{3} + S\cos^2\beta\right) + \alpha_2.$$

As the electric field is perpendicular to the y axis ($E_y = 0$), then we are interesting with these components of the molecular polarizability tensor; the components are not presented.

If $\beta = 0$ one can obtain:

$$\overline{\alpha}_{xx} = (\alpha_1 - \alpha_2)\,\tfrac{1-S}{3} + \alpha_2,$$

$$\bar{\alpha}_{xz} = \bar{\alpha}_{zx} = 0,$$

$$\overline{\alpha}_{zz} = (\alpha_1 - \alpha_2)\,\tfrac{2S+1}{3} + \alpha_2.$$

Let γ_0 is the light beam aperture, then the value of γ varies from 0 to $\gamma_0/2$. The E value is to be averaged on γ and ϕ. Then the cluster energy in the light wave field is equal to:

$$U = U_1(\beta, \phi) + U_2(\beta, \phi) - \frac{1}{2}NF^2A,$$

where $U_1\,(\beta,\varphi)$ is the interaction energy of the molecules in the cluster, $U_2\,(\beta,\varphi)$ is the interaction energy between the clusters:

$$\begin{aligned}
A &= \left[(\alpha_1-\alpha_2)\left(\tfrac{1-S}{3}+S\sin^2\beta\right)+\alpha_2\right]\times B-2\,(\alpha_1-\alpha_2)\,S\times C+\left[(\alpha_1-\alpha_2)\right.\\
&\quad \left.\left(\tfrac{1-S}{3}+S\cos^2\beta\right)+\alpha_2\right]\times D\\
B &= \{\cos\varphi\cdot\cos\left[-arctg\,(tg\varphi\cdot\cos\gamma)\right]\cos\gamma-\sin\varphi\sin\left[-arctg\,(tg\varphi\cdot\cos\gamma)\right]\}^2\\
C &= \sin\beta\cos\beta\big\{\cos\varphi\cdot\cos\left[-arctg\,(tg\varphi\cdot\cos\gamma)\right]\cos\gamma-\sin\varphi\cdot\sin\\
&\quad \left[-arctg\,(tg\varphi\cdot\cos\gamma)\right]\big\}\sin\gamma\times\cos\left[-arctg\,(tg\varphi\cdot\cos\gamma)\right]\\
D &= \sin^2\gamma\cdot\cos^2\left[arctg\,(tg\varphi\cdot\cos\gamma)\right]\\
F &= E_0\tfrac{n_0^2+2}{3},
\end{aligned}$$

n_{o} is the refractive index, N is number of the molecules in the cluster.

If light intensity is relatively low ($I < 10^4$ W m^{-2}) the U_1 and U_2 values can be considered as independent on β. Then for the function of the director distribution on the angles one can obtain:

$$\rho\,(\beta)=C_1\exp\left(-\frac{NF^2A}{2kT}\right),$$

where

$$C_1=\left(\int_0^{\pi/2}\exp\left(-\frac{1}{2}\cdot\frac{NF^2A}{kT}\right)\sin\beta d\beta\right)^{-1}$$

As properties of many LC devices depend on the ratio ρ (90°)/ρ (0°) we derive the following expression:

$$\ln[\rho(90°)/\rho(0°)]=\frac{NF^2(A_{90°}-A_{0°})}{2kT}=\frac{NF^2}{2kT}(\alpha_1-\alpha_2)S(B-D)$$

For the aperture of the light beam γ_0 the $\ln[\rho(90°)/\rho(0°)]$ value should be averaged towards γ:

$$\overline{\ln\left[\rho\,(90°)\,/\,\rho\,(0°)\right]}^{\gamma}=\frac{NF^2}{2kT}\overline{(A_{90°}-A_{0°})}^{\gamma}=\frac{NF^2}{2kT}\,(\alpha_1-\alpha_2)\,S\overline{(B-D)}^{\gamma},$$

where

$$\overline{(B-D)}^{\gamma}=\frac{\int_0^{\gamma_0}(B-D)\sin\gamma d\gamma}{\int_0^{\gamma_0}\sin\gamma d\gamma}.$$

Dependences of $(B - D)$ on γ and of $\overline{(B-D)}^{\gamma}$ on aperture γ_0 are presented in Fig. 2.

If $N = 10^4$ the distribution function is diffused. Comparison with experimental values shows, that $N \geq 10^5$. This value is close to data obtained in [6]. In [10] the N value is a few orders lower. The discrepancy can be explained by using of different methods to obtain the cluster size.

It follows from obtained data that for the low aperture values (up to 40°) the $[\rho(90°)/\rho(0°)]_{\gamma_0=0}/[\rho(90°)/\rho(0°)]_{\gamma_0}$value is changed slightly (less than one order – from 1 to 7) and is increased with γ_0 increase up to 60 at $\gamma_0 = 60°$ and 10^6 at $\gamma_0 = 90°$.

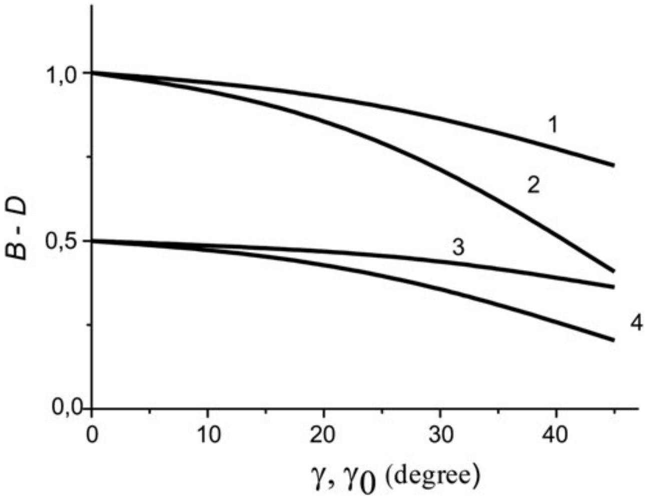

Figure 2. Dependence of (B – D) coefficient on γ (curves 2, 4) and of $\overline{(B-D)}^{\gamma}$ on aperture γ_0 (curves 1, 3) for $S = 1$ (curves 1, 2) and $S = 0.5$ (curves 3, 4)

The dependence of the number of oriented molecules on the irradiation time or absorbed energy E (E is proportional to the irradiation time) can be obtained too:

$$dn = -\chi n dt,$$

$$n = n_0 (1 - \exp(-\chi t)),$$

where n is a number of non-oriented molecules at time instant t; n_0 is a number of non-oriented molecules in the non-irradiated sample, i.e., at $t = 0$. As $E \sim t$ one can obtain:

$$n = n_0 \left(1 - \exp\left(-\chi' E\right)\right).$$

χ and χ' are constants.

Conclusion

The mechanism of dyes and mesogens molecules orientation by laser irradiation is proposed taking into account the anisotropy of molecules optical polarizability. The dependence of the energy of dye and mesogen molecules cluster on the strength of light wave electrical field, anisotropy of molecules optical polarizability, order parameter and number of molecules in a cluster is found. The ratio of clusters distribution function values in parallel and perpendicular directions towards a direction of the laser beam spreading is found. This ratio is shown to change slightly at low angles and to grow essentially with aperture increase attaining 10^2 for 60° and 10^4 for aperture being equal to 90°. The number of molecules in a cluster is estimated. The dependence of the number of oriented clusters on the irradiation energy is obtained.

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