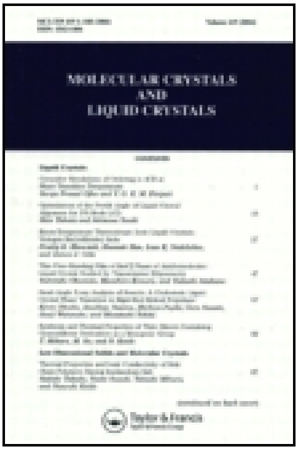

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A Percolation Model to Evaluate the Correlation Length of Dye-Nematic Liquid Crystal Interaction

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Version of record first published: 31 Aug 2006

To cite this article: Anca Alexe-Ionescu, Nicoleta Eseanu, Constanta Dascalu, Andrei Th. Ionescu, Ion Palarie & Cornelia Uncheselu (2005): A Percolation Model to Evaluate the Correlation Length of Dye-Nematic Liquid Crystal Interaction, Molecular Crystals and Liquid Crystals, 437:1, 159/[1403]-168/[1412]

To link to this article: http://dx.doi.org/10.1080/15421400590954399

Mol. Cryst. Liq. Cryst., Vol. 437, pp. 159/[1403]–168/[1412], 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590954399

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The orientation effect of methyl-red (MR) molecules on pentylcyanobiphenyl (5CB) nematic liquid crystal has been investigated in a pump-probe experiment at various concentrations of azo-dye and for different power values of an exciting Ar^+ laser beam. Excited dye molecules reorient the LC molecules within their correlation spheres. There is a percolation probability that the whole LC bulk be reoriented. Analyzing the threshold energy necessary for this percolation in terms of dye concentration, the model allows evaluating the lowest concentration of dye molecules (critical concentration), the correlation length and the quantum efficiency of the reorientation process.

Keywords: dyes; liquid crystals; molecular reorientation; percolation theory

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1. INTRODUCTION

Light induced reorientation effects in dye doped nematic liquid crystals (DDNLCs) have received considerable research interests in recent years [1–11].

In order to explain the observed effects in these systems a multitude of mechanisms has been proposed including dye-induced optical torque [1], dye-induced space charge field [2], photorefractive effect [3,4], light-induced adsorption and desorption of the molecules onto the boundary surfaces [5–7], formation of laser-induced ripple structure on substrate surfaces [8] and order parameter changes [9].

For bulk effects the explanation could be related to the formation of metastable states in the absorption process: an excited electronic structure (singlet or triplet) or a metastable configuration of the nuclear positions (like the *cis*-configuration of an azo-dye). A dye molecule in the metastable state interacts with the surrounding host NLC molecules differently than a dye molecule in the ground state [1].

The formation of the easy axis caused by the anisotropic adsorption of dichroic dye molecules onto the illuminated surface during light irradiation requires an attentive analysis because the adsorption direction depends not only on the light polarization but also on the orientation of the director onto the surface [5,6].

Recently we reported a study of the aligning dye effect on the nematic director for various values of the exciting Ar^+ laser power and we have shown the presence of a threshold effect [10]. The explanation was connected with the nematic local order in the NLC bulk produced by the excited dye molecules. For the assumed spherical oriented zones the radius of alignment depends on the phototransformation of the dye molecules and on the interactions between these molecules and the host NLC molecules. When the exciting laser power is small the oriented zones can be treated as isolated defects in the bulk of NLC. When the power increases (or if the dye concentration is increased) the number of these zones increases too and it appears a critical situation: the distribution of the oriented zones induces a reorientation of the whole NLC cell.

In order to clarify the role of surface structure we investigated the dye aligning effect when the exciting Ar^+ laser beam is impinging through the isotropic surface or through the rubbed one. A significant asymmetry of the signal has been observed [11].

The nature of bulk-mediated photoalignment of DDNLCs has not yet finally elucidated.

In this paper we present a model based on the critical site percolation probability in order to evaluate the correlation length of dye-nematic interaction. We established a linear dependence of the threshold energy E_{th} (necessary to obtain the nematic reorientation) in terms of $1/C$, C being the dye concentration (by weight) of the DDNLC sample. We estimated the critical dye concentration, the correlation length of dye-nematic interaction and the quantum efficiency of the reorientation process.

2. EXPERIMENTS

The experiments were realized by using a standard sandwich glass cell filled with a mixture of 5CB (nematic liquid crystal, clearing point $T_C = 35.2°C$) and azo-dye methyl-red (MR) as a dopant (dye concentrations: 2%, 1.5%, 1%, 0.5% and 0.25% by weight). Their structural formulas are presented in Figure 1.

Methyl red is a photosensitive dye [12]; its intrinsic photochemical processes are: *trans-cis* isomerization and bleaching under the illumination in the absorption band. The absorption spectrum of MR dissolved in 5CB is reported in Ref. [5].

The thickness of the cells was 19 µm (obtained by Mylar spacers). The inner surfaces of the glasses were covered with a thin polymeric film. An easy axis was induced by rubbing one surface. This oriented surface (or passive surface, S_{pas}) imposed the planar orientation of the nematic director for the whole cell in the initial state. The other surface (control surface, S_{con}) is quasi-isotropic and in our experiments the exciting laser beam is impinging through it.

The optical arrangement is shown in Figure 2. The cell was placed normally to the exciting beam of Ar^+ laser (wavelength $\lambda = 476.5$ nm; power P_{exc} was varied between 5 mW and 30 mW). The polarization of the excited beam was established by the polarizer P, the electric vector being horizontal. The probe He-Ne laser beam (wavelength

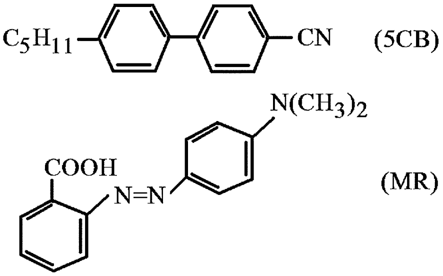

FIGURE 1 Structural formulas of 4′-n-pentyl-4-cyanobiphenyl (5CB) and methyl-red (MR).

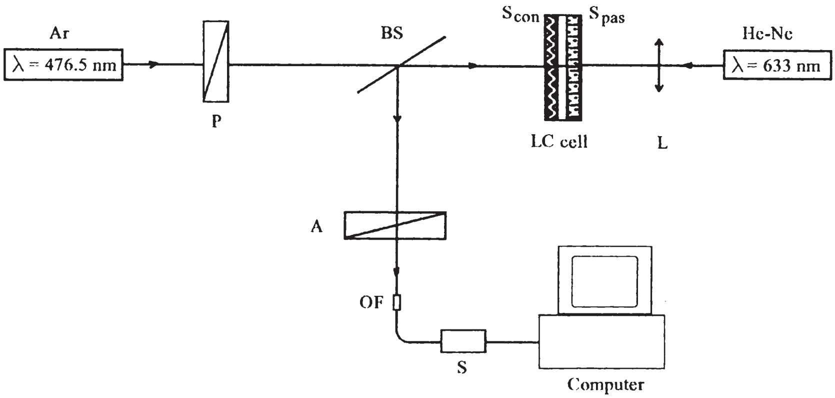

FIGURE 2 Experimental set-up.

$\lambda = 633\,\mathrm{nm}$; power $P_{test} = 1\,\mathrm{mW}$) was focused by a lens L in the same area of the NLC cell. The polarization of the He-Ne beam is 1000:1 for the vertical electric component. Similar experimental set-up was reported in [5], but our geometry is different.

The rubbing direction was parallel with the electric vector of the probe beam. After having passed through the cell the probe beam was deviated by a beam-splitter (BS) and went through the analyzer

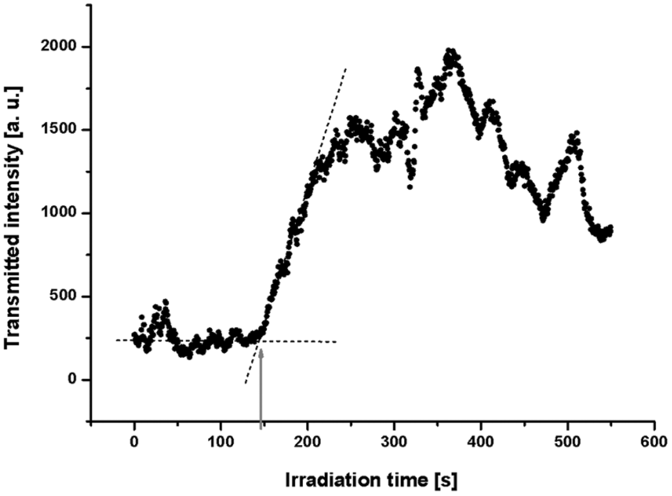

FIGURE 3 Transmitted intensity versus irradiation time for a DDNLC sample containing 5CB + 1.5%MR; $P_{exc} = 20\,\mathrm{mW}$.

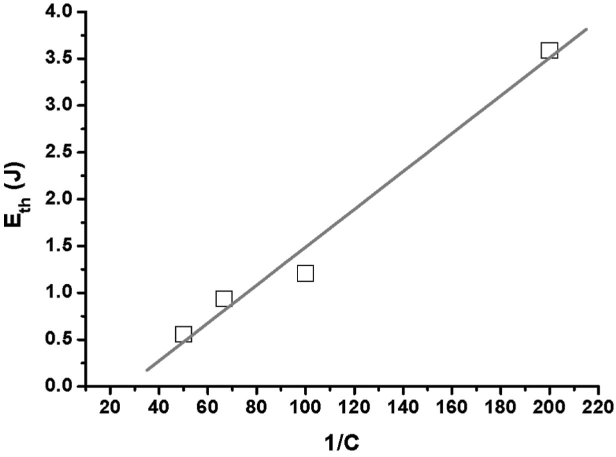

FIGURE 4 Threshold energy versus $1/C$ ($C =$ dye concentration, % by weight).

A which transmission direction was horizontal. The probe beam intensity measurement was performed by an optical fiber (OF) connected with an "Ocean Optics" spectrometer S2000 (S) and a computer. Details about samples and experimental device were presented in Ref. [10].

We measured the time-dependent transmitted intensity of the probe laser beam for various dye concentrations and various exciting laser powers. Figure 3 shows the signal obtained for the sample containing 5CB + 1.5%MR at $P_{exc} = 20\,\mathrm{mW}$ indicating a reorientation process after a threshold irradiation time t_{th}. The value of this time is decreasing if the exciting power P_{exc} (or dye concentration C) is increasing. For dye concentration 0.25% no reorientation effect was observed even for large enough exciting power (30 mW).

Figure 4 presents the experimental values of the threshold energy $E_{th} = P_{exc} \cdot t_{th}$ necessary to obtain the nematic reorientation versus the inverse of the dye concentration ($1/C$).

3. MODEL

Let the whole number N^* of liquid crystal and dye molecules in the sample be divided in N cubic cells (sites):

$$N^* = Nn \tag{1}$$

where n is the average number of molecules in an individual cell. Let p be the probability that a cell contains one dye molecule. The probability that a given cell belong to an infinite cluster $\wp(p)$ is zero if $p < p_c$, where p_c is the so-called critical site percolation probability. If N_a is the total number of active dye molecules then:

$$p = \frac{N_a}{N} = \frac{N_a n}{N^*} = c_a n \tag{2}$$

where c_a is the concentration of active dye molecules respect to the total number of molecules.

For 12-fold coordinated sphere system the critical percolation site probability p_c is 0.20 [13]. Therefore:

$$c_a \geq \frac{p_c}{n} = \frac{0.2}{n} \tag{3}$$

If we change from cubic cells (of number n) to spherical cells, the number of molecules in each cell is $\eta \cdot n$, where $\eta = 0.74$ is the packing factor [13], i.e. the ratio between the total volume of closed packed spheres to the total volume of the box that contains the spheres. Let n_s be the number of molecules in each spherical cell:

$$n_s = \eta n \tag{4}$$

Considering that one of the spheres has a radius of length $2k + 1$ times an average radius, r, of an individual molecule (Fig. 5) the volume of the cell will be:

$$V = \frac{4\pi}{3}(2k+1)^3 r^3 = \eta n \frac{v}{\eta} = nv \tag{5}$$

where v stands for the volume of one molecule (of spherical shape). Simplifying the previous relation one gets:

$$(2k+1)^3 = n \quad \text{or} \quad k = \frac{1}{2}\left(\sqrt[3]{n} - 1\right) \tag{6}$$

Combining Eqs. (3) and (6):

$$k \geq \frac{1}{2}\left(\sqrt[3]{\frac{0.2}{c_a}} - 1\right) \tag{7}$$

or,

$$c_a \geq \frac{0.2}{(2k+1)^3}. \tag{8}$$

The sign "equal" gives the critical concentration c_c of active molecules. (For $k = 2$, $c_c \cong 0.16\%$ and for $k = 3$, $c_c \cong 0.06\%$.) Expressing

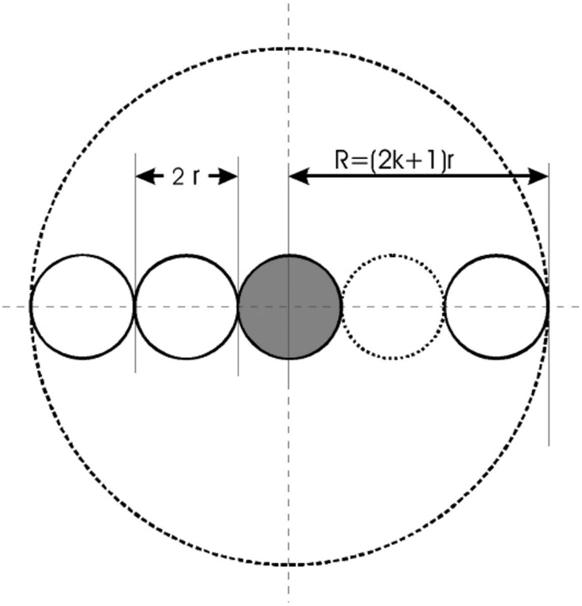

FIGURE 5 The correlation sphere about one dye molecule in terms of the average radius *r* of a "spherical" NLC molecule.

the dye concentration by weight, C, one gets:

$$C = \frac{\mu_d}{\mu} \cdot c \tag{9}$$

where c is the number concentration of dye molecules, μ_d is the molar mass of the dye and μ is the molar mass averaged over the entire system (practically, equal to the molar mass μ_{LC} of the liquid crystal if the dye concentrations are not very high; even more, for 5CB and MR the molar masses are very close $\mu_{LC} = 249$ and $\mu_d = 269$).

The number concentration of active dye is:

$$c_a = c\varepsilon\Phi = c\varepsilon\frac{Pt}{S} \tag{10}$$

where ε is the quantum efficiency and Φ the energetic flux of the exciting Ar^+ laser beam; S is the cross-sectional area of the exciting beam, P is its power and t is the irradiation time. Changing to weight concentration one has:

$$c_a = C\frac{\mu_{LC}}{\mu_d}\frac{\varepsilon}{S}Pt \tag{11}$$

or,

$$C\frac{\mu_{LC}}{\mu_d}\frac{\varepsilon}{S}Pt \geq c_c = \frac{0.2}{(2k+1)^3}. \tag{12}$$

Because $c_a \leq c$, for values of $(\varepsilon/S)Pt > 1$ one should see a saturation of the transmitted He-Ne probe beam. On the other hand, for low values of the product Pt the percolation threshold is not reached, then:

$$C\frac{\varepsilon Pt}{S} \geq C_c, \tag{13}$$

where

$$C_c = \frac{\mu_d}{\mu_{LC}}c_c = \frac{0.2}{(2k+1)^3}\frac{\mu_d}{\mu_{LC}} \tag{14}$$

is the critical concentration (wt).

Rewriting Eq. 13 one gets:

$$Pt \geq \frac{S}{\varepsilon}\cdot\frac{C_c}{C} \tag{15}$$

For those values of Pt smaller than $\frac{S}{\varepsilon}\cdot\frac{C_c}{C}$ no transmitted light is seen, but there is a threshold $(Pt)_{th}$ when the transmitted light starts to increase (Fig. 3) given by:

$$(P\cdot t)_{th} = E_{th} = \frac{S}{\varepsilon}\cdot\frac{C_c}{C}. \tag{16}$$

Identifying the moment t_{th} and multiplying it with the power P of the exciting laser beam, for cells with different dye concentration, the graph of E_{th} in terms of $1/C$ should be a straight line, as can be seen in Figure 4.

4. DISCUSSION

Diminishing the concentration C the effect should no longer be seen for $C < C_c$ that is the graph (as in Fig. 4) should stop at a certain value of $1/C$. Actually, in Figure 4 the last point (at upper right) corresponds to $C = 0.5\%$ (wt.). Having tried with a smaller concentration $C = 0.25\%$, no effect was observed, so one can conclude that:

$$2.5\cdot 10^{-3} \leq C_c \leq 5\cdot 10^{-3}. \tag{17}$$

Coming back to Eq. 14:

$$2.5 \cdot 10^{-3} \leq \frac{\mu_d}{\mu_{LC}} \frac{0.2}{(2k+1)^3} \leq 5 \cdot 10^{-3} \tag{18}$$

or,

$$1.25 \leq k \leq 1.70. \tag{19}$$

In other words, the oriented dye molecules can no longer command the order of the liquid crystal if there will be, on average, more than four liquid crystal molecules (in line) between two dye molecules.

Knowing the critical concentration C_c and the cross-sectional area S of the Ar^+ laser beam, from the slope, s, of the line in Figure 4, one can estimate the quantum efficiency ε:

$$\varepsilon = \frac{SC}{s}. \tag{20}$$

The linear regression in Fig. 4 gives $s = 0.02\,J$, therefore:

$$3.5 \cdot 10^{-6} \frac{m^2}{J} \leq \varepsilon \leq 7 \cdot 10^{-6} \frac{m^2}{J}. \tag{21}$$

5. CONCLUSIONS

By measuring the optical transmission in a dye doped nematic sample excited by an Ar^+ laser beam, we estimated the critical concentration of dye molecules for which the nematic reorientation appears. In our model this concentration is related to the critical percolation probability that the local reorientation induced by the excited dye molecules extends on the whole bulk.

In terms of the energetic flux of the exciting beam the threshold energy E_{th} is inverse proportional to the concentration C of the dye. The ultimate point on the graphic line gives a higher limit of the critical concentration of dye molecules. The experimental data are in good agreement with the established dependence $E_{th} = f(1/C)$.

To have a better estimation, a set of different dye concentrations about the critical one should be prepared in smaller steps. Even if these steps are very small there is always only an estimation of the critical concentration because of the simplifying assumptions made: both dye and nematic liquid crystal molecules have been considered spheres of equal radii and the system is imagined as a 12-fold coordinated crystal.

By using the estimated values of the critical dye concentration we evaluated the correlation length of dye-nematic interaction and the quantum efficiency of the reorientation process in a DDNLC sample.

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