Study of the on – off – on dye doped nematic irradiation in a pump-probe experiment

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The irradiation with an Ar^+ laser beam of the cells filled with 5CB doped with MR has been performed in a series of the type on – off – on in a pump-probe experiment. In the first period of irradiation the recorded probe signal of a He-Ne laser beam is quasi-constant at beginning of the time and then increased with the irradiation time. A jump and a delay were observed at the end of the first irradiation period. In the off period of irradiation the signal is quasi-constant. A jump and a delay were also observed at the second irradiation. These experimental results were explained based on the trans-cis and cis-trans isomerisation of the MR molecules and on the fact that the trans isomer has an absorbance for the red light (He-Ne laser) less than that corresponding to the cis isomer.

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1. Introduction

The alignment surface of liquid crystal (LC) molecules is very important in LC displays. [1] If the alignment of LCs is done by rubbing a polyimide/polymer film coated on glass plates, there can appear some problems due to static electricity, dust particles and other residues on the rubbed surface.

A new technique, called photoalignment, permits the alignment and subsequent realignment of the director of the cell filled with LCs [2, 3]. The photoalignment technique is a non-contact method that does not induce a mechanical stress on the polymeric surface. It was found that the presence of a small quantity of absorbent dye (less than 1% wt) dissolved in a nematic liquid crystal (NLC) greatly amplifies the orientational response of the LC [4,5].

The dye was azo- or antraquinone-derivates present a great photostability. The majority of them have two stable configurations: the trans and cis forms. Within the limit of small concentrations and small light intensity, the two isomers act as independent dopants giving independent contributions in the reorientation process. An explanation of the dye contribution could be the following: many dye molecules have π delocalized orbitals and by dissolving them in LCs or polymers leads to aligning phenomena under linearly polarized laser light.

Another effect is the light-induced dye adsorption [6, 7] leading to the accumulation of dye molecules at the bounding plates of the cell, which can also play a role in the surface-induced reorientation.

Among other dye-doped liquid crystals (DDLCs) methyl-red (MR)-doped NLCs represent a very interesting system for studying photoalignment. Under proper irradiation with blue-green light, MR molecules are adsorbed on the surface of the substrate, reorienting the LC molecules into a permanent LC configuration [8]. The surface morphology of the adsorbed substrate has been studied by Lee *et al* [9] and three different morphologies have been observed - a homogeneous and fine layer of adsorbed dyes, a layer with microgrooves and an inhomogeneous ribbon like and rough adsorbed layer. When the weak-intensity regime is used, the first and second types of layers dominate in the early and late stages, respectively, tending to reorient the LCs perpendicular and parallel to the polarization direction of the pump beam. The last type of layer dominates in the strong-intensity regime, severely disturbing the orientation of the LCs. Recently, Pălărie *et al* [10-13] reported on laser-induced ripple structures in DDLC films in the high-intensity regime.

In this work, we present an experimental study on the influence of the on- off- on Ar^+ beam irradiation on the photoalignment of the MR doped NLC.

The photo-controlled alignment effect is studied for four pump powers: 2, 3, 25 and 30 mW.

The evolution of the transmitted intensity of the probe beam during irradiation was explained taking into account the photoalignment effect and and cis-trans transition of MR molecules in the off sequence of irradiation.

2. Experimental procedure

In this study, experiments were realized at a temperature of 25^{0} C by using standard sandwich glass cells filled with a mixture of a NLC 4'-n-pentyl-4-cyanobiphenyl (5CB) and MR azo-dye as a dopant (the dye concentration was 2% wt). Their structural formulae are presented in Fig. 1.



Fig. 1. The structures of 5CB and of MR in the trans- form.

5CB was purchased from Merck Ltd (Pool, GB). MR is a photosensitive dye purchased from Aldrich. Its intrinsic photochemical process is rotation, trans-cis isomerization and bleaching under illumination in the absorption band. The thickness of the cells is 23 μ m (obtained by Mylar spacers). The inner surfaces of the glass plates were previously covered with a thin polymeric film by spin coating method. The monomer, polyvinyl alcohol (PVA), was dissolved in water at a concentration of 3% wt. The PVA solution was spin coated on the glass plates, baked at 120 0 C for 60 min and cooled at room temperature.

NLC in contact with a solid surface tends to orient in a well-defined manner, depending on the orienting surface properties. In the absence of bulk constraints, this direction is called the easy axis.

For our measurements we used asymmetric cells which an easy axis was induced by rubbing one surface (S_R , reference surface) in a unique direction. A planar alignment of the cell was imposed by the inner rubbed reference surface, S_R . The other surface (command surface, S_C) was quasi-isotropic and its position in the setup was toward the pump laser beam (Fig. 2).



Fig. 2. The experimental setup: Ar^+ laser - INNOVA 308C; $\lambda/2$ - half-wave plate; P_1 , P_2 - polarizers Glan-Thomson; A - analyzer Glan-Thomson; BS - beam splitter, S_C - command surface; S_R - reference surface; LC cell - liquid crystal cell; He-Ne laser - 1 mW; OF optical fiber; S - Ocean Optics Spectrometers S2000; PC - personal computer.

The optical arrangement used for pump-probe experiment is schematically shown in Fig. 2 and described in [10-12]. The cell was placed perpendicular to the exciting beam of Ar⁺ laser (of type INNOVA 308C) working at λ =476.5 nm. The pump power P_{exc} (measured in front of the command surface, S_C, with a power meter, Field Max II-Top from Coherent) was varied between 2 and 30 mW. The diameter of the Ar⁺ laser beam on the cell was ~2 mm and the mean intensity of the pump beam in the irradiated areas had the values 64, 96, 800 and 960 mW cm⁻² (corresponding to 2, 3, 25 and 30 mW, respectively). The direction of rubbing on S_R was parallel to the polarization direction of the beam emerging from the Ar^+ laser (vertical in the setup). Pump beam polarization could be rotated with 90° using the polarizer P₂ and a half-wave plate ($\lambda/2$) oriented at 45° with respect to the vertical direction. The polarization direction of the He-Ne laser beam was established by the polarizer P₁ that had a vertical transmission direction (parallel to the easy axis of the sample). The spot size of the probe ($\lambda = 633$ nm, power $P_{probe} \sim 1$ mW) matched the one of the pump light on the cell.

After passing through the cell, the probe beam was deflected by a beam splitter (BS) and sent through the analyzer (A) whose transmission direction was horizontal. The measurement of the probe beam intensity was made by an optical fiber (OF) connected to an Ocean Optics spectrometer S2000 (S) and a computer (PC). The intensity of the transmitted probe beam was recorded during the irradiation of the two cells with 2 mW and 3 mW, in a series of the type on - off -on. For these cells, the first irradiation period is 500 s, the off period is 300 s and the second irradiation period is 400 s. For other cells, different series of irradiation have been performed.

3. Results and discussion

In the Figs. 3 and 4 the transmitted intensity of the probe beam is reported, in on- off- on experiment for 2 and 3mW, respectively.



Fig. 3. The transmitted intensity versus irradiation time for 2 mW.



Fig. 4. The transmitted intensity versus irradiation time for 3 mW.

We remark that in the first sequence of the irradiation the signal is constant at the beginning of the irradiation time and then it increased with the irradiation time.

Before the sequence on-off-on, the intensity of the transmitted light is first constant, than increases with the irradiation time. This time corresponds to the beginning time of the ripple structure formation is explained by existing the vertical orientation of the easy axes and by the anchoring energy induced in the rubbing process.

After that, during the irradiation almost all MR molecules suffer the trans cis isomerisation, are absorbed on the microgrooves structure and the transmitted signal is quasi-constant. The microgrooves structure induces the rotation of the nematic director on the command surface, S_C in agreement with our previous results reported in [10-12]. Thereby, a permanent twist nematic structure by irradiation of the cell with the Ar^+ pump beam has been induced.

When the Ar^+ laser beam is switched off, a jump of the recorded signal is present and a new constant value of the transmitted intensity is reached, as shown in Fig. 4. The jump of the intensity could be most probably induced by cis-trans isomerisation of the MR molecules. In the trans form, the probe radiation is less absorbed than in the cis form [14]. After 300s the AR⁺ laser is switched – on, the trans –cis isomerisation occurs and the transmitted intensity is turning - back to the same value at which the irradiation was stop.

A similar evolution of the transmitted intensity has been obtained for pump power of 25 and 30 mW (Fig. 5 and 6).



Fig. 5. The transmitted intensity versus irradiation time for 25 mW.



Fig. 6. The transmitted intensity versus irradiation time for 30 mW.

After an irradiation of 9 min at a pump power of 25 mW a permanent twisted nematic structure has been induced and the rotating angle has the values 83 0 C. [10, 12]. For the power of 30 mW a twisted angle can not be measured in the center of the irradiated zone due to a rapid and random aggregation of MR molecules.

4. Conclusions

In this study, we investigated the irradiation of the cells filled with 5CB doped with MR in a pump-probe experiment. We used four pump powers 2, 3, 25 and 30 mW from an Ar⁺ laser and the irradiation has been performed in a sequence of the type on – off – on. When the irradiation is stopped, we remark a jump of the recorded probe beam signal. The explanation of this jump could be based on transcis isomerisation of MR molecules. In the trans form the absorbance of the red light (He-Ne laser beam) is less than that for the cis form. When the Ar^+ laser beam is on again the signal increases again with the irradiation time.

This study demonstrates the possibility to control the intensity of the transmitted probe beam by a series of irradiation of the type on - off - on. Also, the effect of trans-cis and cis-trans isomerisation of MR molecules on recorded data has been observed.

Further studies are needed in order to give a quantitative explanation of this experimental result.

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