

Manipulation of anchoring strength in an azo-dye side chain polymer by photoisomerizationL. T. Thieghi,¹ R. Barberi,² J. J. Bonvent,³ E. A. Oliveira,¹ J. A. Giacometti,⁴ and D. T. Balogh⁵¹*Instituto de Física, Universidade de São Paulo, P.O. Box 66318, São Paulo 05315-970, SP, Brazil*²*INFN Research Unit, Physics Department, University of Calabria, via Pietro Bucci, 87036 Rende (CS), Italy*³*Universidade de Mogi das Cruzes, Avenida Dr. Cândido Xavier de Almeida Souza 200, CEP 08780-911, Mogi das Cruzes, SP, Brazil*⁴*Faculdade de Ciências e Tecnologia, Universidade Estadual Paulista, Presidente Prudente, 19060-900, SP, Brazil*⁵*Instituto de Física de São Carlos, Universidade de São Paulo, P.O. Box 369, 13560-970 São Carlos, SP, Brazil*

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The generation of surface anisotropy by photochemical means has been proposed as an attractive method to align liquid crystals. In this paper, we present an experimental study of the alignment induced on a liquid crystal by a polymer film containing azo-dye groups in the side chain. Optical measurements were performed in nematic liquid crystal cells to determine the azimuthal and zenithal anchoring strengths as a function of the irradiation energy and chromophores concentration. It was observed that the director tends to align perpendicular to the polarization direction of the incident light and the orientation process consists essentially of a rotation of the director in the plane parallel to the boundary surfaces. However, the concentration of azo-dye groups in the polymer film must exceed a minimum value to get a macroscopical effect on the liquid crystal alignment. It is shown that the azimuthal anchoring strength can be varied two orders of magnitude by controlling the irradiation energy and azo-dye concentration.

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I. INTRODUCTION

Liquid crystals (LC) are materials with anisotropic properties that are very useful in the design of electro-optical devices such as the liquid crystal displays. The principle of operation of such devices combines bulk properties (such as the birefringence, elastic constants, dielectric anisotropy, etc.) and surface interactions. The delicate balance between bulk and surface interactions determines the performance of these devices. Therefore, controlling the alignment of the liquid crystal molecules is a subject that has attracted experimental and fundamental studies [1–3]. Although there is a variety of interactions responsible for the LC alignment [4], two major factors can be identified to influence the anchoring of LC molecules on a solid substrate: the anisotropic intermolecular interactions between the substrate and the liquid crystal, and the steric interactions due to the substrate topography.

In fact, many surface treatments have been proposed to promote the alignment of LC molecules based on mechanical or chemical processes applied to the substrate [4]. An attractive alternative to such processes is the generation of surface anisotropy on a polymer film by photochemical means [5–7]. In recent years a promising photoalignment process has been proposed, taking advantage of the orientational changes promoted by light in photochromic molecules and the amplification of such effect by the liquid crystal due to its supramolecular order leading to remarkable changes in orientation direction of the LC molecules [6].

Azo-dye molecules undergo reversible structural changes from *trans* to *cis* configuration upon illumination, the longer the wavelength the greater the proportion of *trans* configuration [7]. Thin films of polymer containing azo-dye groups covalently attached to the main chain have been used to obtain photoalignment effects in liquid crystals. When the polymer is illuminated with polarized light, the absorption prob-

ability is greater for molecules with the transition moment parallel to the direction of the polarized light. The *trans-cis* isomerization reduces the molecular volume as the excited molecule relaxes to a random orientation [7,8]. After some time of irradiation, there is a depletion of transition moments parallel to the direction of polarized light due to the selective absorption of light and an anisotropy is developed in the film leading to a homogeneous alignment of the liquid crystal in contact with the film. The threshold for obtaining azo-dye photoalignment depends on the particular molecular structure of the polymer and also on the architecture of the film (self-assembly, Langmuir-Blodgett, etc.). Some theoretical studies have been dedicated to investigate the photoalignment induced on the LC in phenomenological approaches, trying to get a relationship between experimental parameters (such as induced birefringence, twist angle, etc.) and the orientational distribution of chromophores in the polymer film [9–12].

In this work, we present an experimental study of the photoalignment induced on a nematic liquid crystal by a polymer film containing azo-dye groups (DR-13) in the side chain. The polymer film was irradiated with polarized light from an argon laser operating in the wavelength of 514.5 nm and the developed anisotropy was probed by a He-Ne laser beam. The excitation wavelength was selected to maximize the absorption of the polymer and four different concentrations of azo-dye groups in the polymer were used. Optical measurements were performed in nematic liquid crystal cells using as boundary surfaces glass plates coated with the polymer film to determine the azimuthal and zenithal anchoring strengths as function of irradiation energy and concentration of chromophores in the polymer film.

II. THEORETICAL CONSIDERATIONS

Let us consider a nematic liquid crystal between two boundary surfaces (1 and 2) parallel to x - y plane, with azi-

muthal and zenithal anchoring strengths W_{φ_i} and W_{θ_i} ($i = 1, 2$), respectively. The orientation of the easy axes with respect to the reference frames are given by the angles; φ_{\min_i} , θ_{\min_i} , ($i = 1, 2$), where φ_{\min_i} is measured with respect to the x axis, θ_{\min_i} is the tilt angle, measured with respect to the x - y plane and the actual orientation of the director is given by the angles φ and θ . The equilibrium configuration of the director can be determined from the minimization of the distortion energy in the cell, taking into account the suitable boundary conditions. We will discuss below two particular cases that will be useful for the determination of the azimuthal and zenithal anchoring strength at one of the surfaces.

A. Azimuthal anchoring strength

Assuming a strong planar anchoring at surface 1 the boundary conditions are then $\theta_{\min_1} = \theta_1 = 0$, $\varphi_{\min_1} = 0$, and $W_{\varphi_1} \rightarrow \infty$. Such condition can be achieved using a SiO_x plate (obtained under specific evaporation conditions). With surface 2 coated with the photochromic polymer, we consider that the photoalignment induces a rotation of the easy axis in the polymer film, resulting in a pure twist deformation of the LC sample through the cell thickness d (z axis). The orientation of the easy axis at the second surface, with respect to the reference frame is characterized by; $\theta_{\min_2} = 0$, $\varphi_{\min_2} = \Phi$, $\varphi_2 > 0$, and a finite anchoring strength W_{φ_2} .

The minimization of the free energy [13,14],

$$\frac{F}{A} = \frac{1}{2} \int_0^d K_{22} \left(\frac{d\varphi}{dz} \right)^2 - \frac{1}{2} W_{\varphi_2} \sin^2(\varphi_2 - \Phi), \quad (1)$$

gives the director configuration in the sample: $\varphi(z) = (\varphi_2/d)z$, where K_{22} is the twist elastic constant. From the balance of the torques in the boundary surface, we get

$$W_{\varphi_2} = \frac{2K_{22}\varphi_2}{d \sin[2(\varphi_2 - \Phi)]}. \quad (2)$$

The above equation relates the azimuthal anchoring strength at the photopolymer surface, W_{φ_2} , and the twist angle φ_2 which can be experimentally determined as will be described in Sec. III B.

B. Zenithal anchoring strength

For the determination of the zenithal anchoring strength a hybrid cell can be used, where one of the surfaces (1) has a strong homeotropic anchoring and the other (2) a weak planar anchoring [14]. At surface 1, the boundary conditions are expressed by $W_{\theta_1} = \infty$ and the orientation of the easy axis is characterized by, $\theta_{\min_1} = \theta_1 = \pi/2$. For the second surface, with planar anchoring, the orientation of the easy axis is given by, $\theta_{\min_2} = 0$ and the zenithal anchoring strength W_{θ_2} is finite.

In the one-constant approximation [13], $K = K_{11} = K_{33}$, the minimization of the free energy allows one to get the equilibrium condition at the boundary surface, expressed by

$$K \left[\frac{d\theta}{dz} \right]_{z=d} - \frac{1}{2} W_{\theta_2} \sin(2\theta_2) = 0, \quad (3)$$

where θ_2 is the tilt angle induced to nematic liquid crystal (NLC) molecules in the photopolymer film. Applying the boundary conditions in the above results in a relation between the zenithal anchoring strength W_{θ_2} and the tilt angle θ_2

$$W_{\theta_2} = \frac{2K\theta_2}{d \sin(2\theta_2)}. \quad (4)$$

Experimentally, we can have access to the phase shift δ introduced in the probe beam when crossing the hybrid cell, of thickness d . The phase shift can be related to the tilt angle θ_2 , considering the director distortion in the cell, by the following equation [15]:

$$\frac{\lambda \delta}{2\pi d} \frac{1}{n_o} + 1 = \frac{\int_0^{\theta'_2} \sqrt{\frac{1 - k_a \sin^2 \theta'}{1 - R \sin^2 \theta'}} d\theta'}{\int_0^{\theta'_2} \sqrt{1 - k_a \sin^2 \theta'} d\theta'}, \quad (5)$$

where $k_a = 1 - (K_{11}/K_{33})$ is the elastic anisotropy, K_{11} and K_{33} , are the splay and bend elastic constants, respectively, $R = 1 - (n_o/n_e)^2$ is the optical anisotropy, with n_o and n_e equal to the ordinary and the extraordinary refraction indexes, respectively, λ is the laser wavelength and $\theta'_2 = \pi/2 - \theta_2$. Using a software (MATHEMATICA), we can plot δ as a function of θ'_2 , and for each measured value of δ we obtain the corresponding value of tilt angle θ_2 . The simulations were performed considering two situations: with elastic anisotropy $k_a = 0.36$ and with $k_a = 0$. With the values of θ_2 , inserted in Eq. (5), we calculate the zenithal anchoring strength.

III. EXPERIMENTAL METHODS

A. Materials

The photopolymer used (PHEMA-DR13) is a random copolymer of methacrylate derivatives [16] containing a chromophore covalently attached to the main chain [Fig. 1(a)]. The concentration of the comonomer containing the chromophore was determined by UV-Vis measurements [17]. In this study polymer with four different concentrations of chromophores were used: 6%, 17%, 38%, and 60% by weight. In the visible region of the spectrum the photopolymer exhibits a maximum absorption for $\lambda \approx 500$ nm, as is shown in Fig. 1(b). The nematic liquid crystal used is the 4-pentyl-4'-cyanobiphenyl usually known as 5CB (K15-Merk). Glass plates for optical microscopy (corning) were coated by spin coating, and baked for ≈ 1 h at 90°C to evaporate the solvent. Such plates were used to build cells where the liquid crystal was inserted by capillarity.

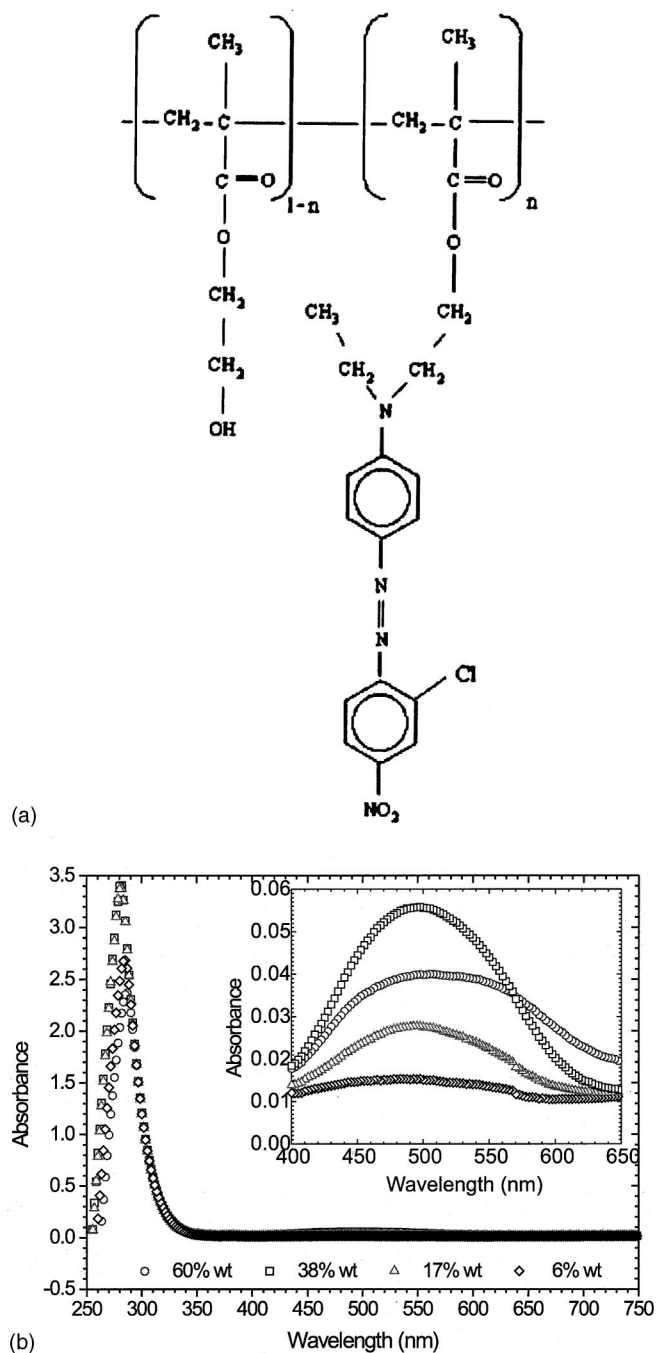


FIG. 1. (a) Structure of the photopolymer PHEMA-DR13 with the azo dye as lateral group. (b) Absorption spectrum for PHEMA-DR13.

B. Twist angle measurements

The determination of azimuthal anchoring strength was performed by measuring the twist angle induced by photoalignment in a planar cell, where one of the surfaces was coated with the photopolymer and the second surface was evaporated with SiO_x to induce strong planar anchoring. The cell was mounted with the plates parallel to each other (~30 μm thick), using mylar spacers, hence the initial orientation of the director in the sample is a planar texture and it is induced by the flow direction and by the evaporated

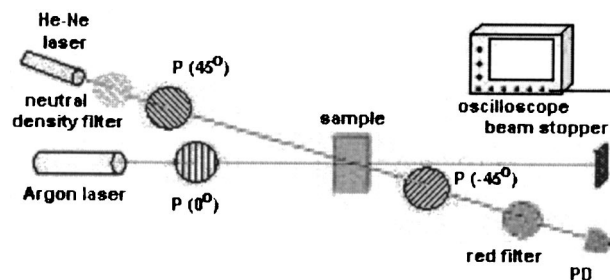


FIG. 2. Experimental arrangement for twist angles measurements.

surface. The cell thickness *d* was determined by measuring the optical path difference Γ of a polarized beam crossing the sample with a compensator: $\Gamma = d\Delta n$, where $\Delta n \approx 0.1$ is the birefringence of the nematic liquid crystal in a planar cell.

The photoalignment was achieved by irradiating the cell, with a linearly polarized argon laser as excitation beam, operating in the wavelength $\lambda = 514.5$ nm, with incident power of 1.2 mW, at normal incidence. During the experiments the cells' temperature was checked and no heating was observed. The transmittance of the sample was monitored by a He-Ne probe laser crossing the sample at near normal incidence, which intensity was attenuated by a neutral filter (6.95 μW). The polarization direction of the excitation beam polarization was set at an angle of 45° with respect to the probe beam polarization direction. A red filter was positioned in front of a photodetector connected to an oscilloscope, to assure that the signal is due only to the probe beam. The experimental setup is schematically represented in Fig. 2. The sample is initially positioned with the nematic director parallel to the probe beam polarization direction, which corresponds to a minimum transmittance. Due to the photorientation of the azo-dye groups a reorientation of the director occurs, that tends to align perpendicular to the polarization direction of the excitation beam, resulting in an increasing of the transmittance of the sample. The rotation of the director, or the twist angle, can be measured by rotating the analyzer until the minimum transmittance is recovered. The twist angle is determined as a function of the irradiating time, for a fixed incident power.

C. Pretilt angle and thickness measurements

To investigate if the photoalignment of the dye groups induces a pretilt angle on the NLC molecules in contact with the polymer film [18] a cell (~30 μm thick) was mounted in the antiparallel configuration using two identically irradiated polymer coated substrates and mylar spacers. Such antiparallel configuration leads a homogeneous aligned sample, even if any pretilt angle is present.

The photoalignment was probed by a linearly polarized He-Ne laser beam and the sample was placed in a rotatory stage, to allow varying the incidence angle Ψ . Since the light is generally elliptically polarized after crossing the sample, a quarter wave plate is used to recover the linear polarization. The phase shift δ introduced by the sample can be obtained by splitting the probe beam into two beams: one as reference and the other crossing the sample. A rotatory analyzer plate

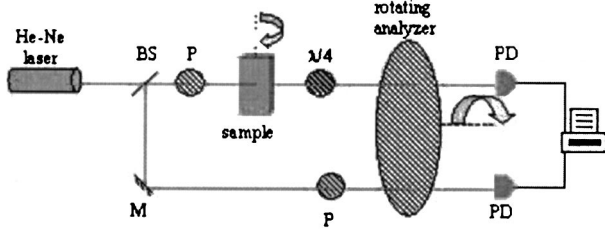


FIG. 3. Experimental arrangement for pretilt angles and thickness measurements.

allows to modulate the two beams in order to measure the phase shift, as is shown in Fig. 3. The relative orientation of the polarizers was selected to have initially $\delta=0$. Assuming that the pretilt angle of the molecules in contact with the polymer film is ϵ (measured with respect to the plane of the surface) and that there is not a distortion along the thickness, the phase shift introduced by the sample when the probe beam crosses it at an incidence angle Ψ is given by

$$\delta = \frac{2\pi d}{\lambda} \left[\frac{(n_o^2 - n_e^2)}{n^2} \sin \epsilon \cos \epsilon \sin \Psi + \frac{n_o n_e}{n^2} \sqrt{n^2 - \sin^2 \Psi} - \sqrt{n_o^2 - \sin^2 \Psi} \right], \quad (6)$$

where $n^2 = n_o^2 \cos^2 \epsilon + n_e^2 \sin^2 \epsilon$, and λ is the laser wavelength (632.8 nm). By measuring the phase shift as a function of the incident angle, and fitting the experimental results using the above equation, one can determine simultaneously both d and ϵ .

D. Measurements for determining the zenithal anchoring strength

The zenithal anchoring strength of the NLC molecules at the photopolymer substrate was obtained by using a hybrid cell ($\sim 23 \mu\text{m}$ thick), where one of the plates was coated with DMOAP (*n*-*n*8-dimethyl-*n*-octadecyl-3-aminopropyltrimethoxysilyl chloride) to obtain a strong homeotropic anchoring and the second plate was coated with the polymer film. The cell was then irradiated, with the argon laser beam, linearly polarized and the tilt induced to the NLC molecules in contact with the polymer film was determined by measuring the phase shift introduced by the sample when the probe beam crosses it at normal incidence, using the same setup described in Sec. III C.

IV. RESULTS AND DISCUSSIONS

A. Qualitative aspects

It is known that when the LC is introduced in a cell by capillarity, the flow induces a certain orientation, with the molecules parallel to the flow direction [19]. However, if there is no easy axis in the boundary surfaces, such effect is not stable and after some seconds the orientation disappears. In the hybrid cells (described in Sec. III D), we observed that the orientation induced to the NLC by capillary flow is very

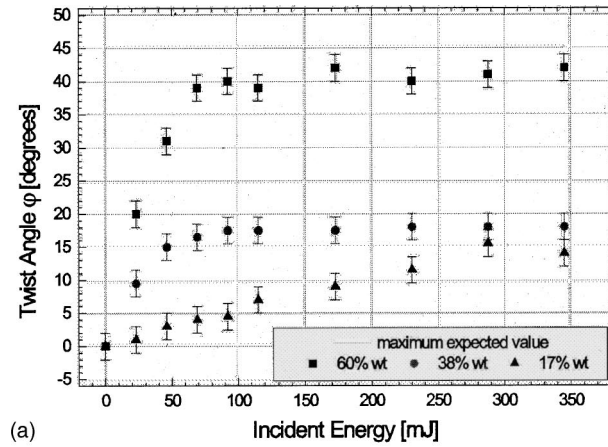
stable, specially for the polymer films with lower concentration of azo-dye groups (6% and 17% in weight). When the sample is heated up to 40°C , above the transition to the LC isotropic phase and kept at such temperature during few minutes, the orientation induced by flow is recovered when the sample is cooled down to the nematic phase. We speculate that the alignment induced by flow is due to the lateral azo-dye groups, that have some mobility in the polymeric matrix and could be oriented by flow. Although the number of azo-dye groups is smaller for low concentrations, the mobility is larger, and this would be responsible for the higher quality in the orientation induced to the nematic liquid crystal. Another possibility for this is the molecular anisotropic adsorption of the NLC molecules on the polymer film [20].

The photoalignment is stable for a long period of time (several months), however a new orientation can be induced to the cell, by irradiating the cell with a different polarization direction. The thermal stability of the photoaligned cell was also investigated by heating it above the *N-I* transition temperature. By cooling the sample back to the nematic phase, the initial photoinduced orientation is recovered. Nevertheless, if the cell is heated up to 90°C , approaching the glass transition of the polymer, the NLC alignment is destroyed and a new irradiation with the previous conditions is not sufficient to induce a new photoalignment: the process is slower and the orientation is not homogeneous.

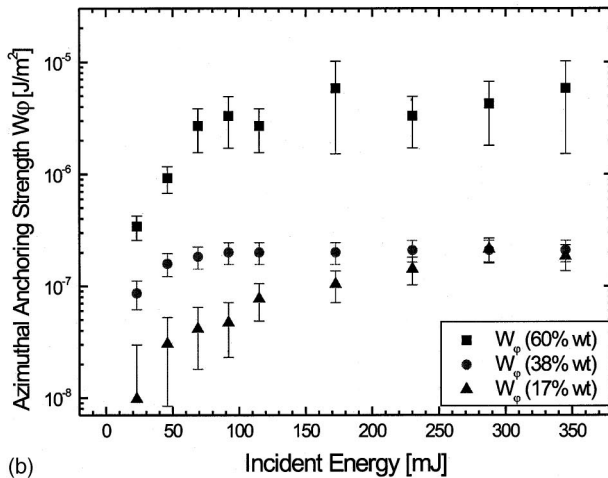
B. Azimuthal anchoring strength

In order to determine the azimuthal anchoring strength we performed measurements of the twist angle induced by photoirradiation to the planar cells, as described in Sec. III B. No photoalignment effect was observed for polymer films containing 6% in weight of azo-dye groups, even for an incident power as high as 7.1 mW. In Fig. 4(a) are shown the experimental values of the twist angle determined as a function of the exciting light energy for cells with different dye concentrations, for an incident power of 1.2 mW. One can clearly observe that the twist angle increases with increasing irradiation energy, until a saturation level is reached. The maximum twist angle obtained for 17% and 38% is almost the same, although the concentrations are different by a factor 2. This may be attributed to the difference in the cell thickness: the cell with 17% of azo dye is thicker than the two others.

The values of twist angle were inserted in Eq. (2) to determine the azimuthal anchoring strengths, that are presented in Fig. 4(b), as a function of the irradiation energy, for the above mentioned cells. We observe that the azimuthal anchoring strength increases with increasing irradiation energy, tending to a limiting value. The energy required to reach the limiting value is approximately the same for the polymer with 38% and 60% of azo-dye: $\approx 80 \text{ mJ}$ and it is about 300 mJ for the less concentrated one. It is interesting to note that the maximum azimuthal anchoring strength is approximately the same, $\approx 10^{-7} \text{ J/m}^2$ for azo-dye concentrations of 17% and 38%, although this condition is reached faster for the more concentrated one. We can also notice that the anchoring strength can vary from 10^{-8} J/m^2 up to $\sim 10^{-6} \text{ J/m}^2$ de-



(a)



(b)

FIG. 4. (a) Twist angles induced by linearly polarized light in function of the exposure energy for three different lateral group concentrations. (b) Azimuthal anchoring strengths as function of exposure energy for three different lateral group concentrations.

pending on the azo-dye concentration in the photopolymer film or on the incident energy.

C. Pretilt angle

The influence of the photoalignment on the pretilt of the NLC molecules was investigated using cells built with the two boundary surfaces coated with the photopolymer previously irradiated as described in Sec. III C. The measured values of phase shift δ , as a function of the incidence angle of the probe beam, are presented in Fig. 5 for 60% of azo dye in the polymer film. The fitting of the experimental curve was performed using Eq. (5) with d and ϵ as fitting parameters.¹ The pretilt angles obtained from this procedure are very small, less than 0.01 rad, (or 1°), for all concentrations of azo dye in the polymer film, indicating that the director rotates in the plane of the film, practically without any pretilt.

D. Zenithal anchoring strength

Using a hybrid cell with a homeotropic alignment in one of the surface and a initially planar anchoring in the photo-

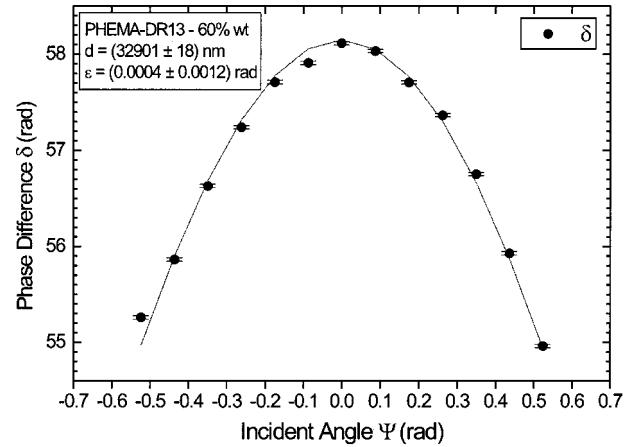


FIG. 5. Determination of pretilt angle for 60% of azo-dye concentration in the polymer film. The solid curve corresponds to the best fitting of Eq. (6) to the experimental points.

polymer, we performed measurements of the phase shift introduced in the probe beam by the nematic sample, for normal incidence. The tilt angle θ_2 was then determined from Eq. (5). The values obtained for tilt angles are between 4° and 19° indicating that the molecules in contact with the polymer are tilted with respect to the normal. It is important to remind that, these results differ from the previous results for the pretilt angle, because in this case, in the second boundary surface the alignment is homeotropic, and even before irradiating the sample, there is a tilt of the molecules, due to the elastic distortion introduced by the different alignments imposed in each surface.

Inserting the values of θ_2 and the thickness d in Eq. (4), we obtain the zenithal anchoring strength W_θ for the cells before and after the photoalignment, and the resulting values are listed in Table I, for $k_a = 0.36$. The values obtained with $k_a = 0$ differ from the listed values in the second significative numeral. Within the uncertainty of our measurements, we observe that both the tilt angle and the zenithal anchoring strength are not significantly affected by the irradiation. The magnitude of anchoring strength is typically 10^{-7} J/m^2 which corresponds to a very weak zenithal anchoring strength [21].

V. CONCLUSIONS

It was observed that flow of NLC when it is introduced in the cell, induces an alignment of good quality, and in contrast to the usual observed flow alignments it is very stable. We

TABLE I. Tilt angles (in degrees) and zenithal anchoring strengths (in J/m^2) as a function of the azo-dye groups concentration in the polymer film (in weight %).

Azo-dye	Nonirradiated		Irradiated	
Concentration	θ_2	$10^{-7} W_\theta$	θ_2	$10^{-7} W_\theta$
17%	7	3.4	8	3.5
38%	18	3.3	10	3.2
60%	4	3.2	10	3.3

¹The fitting was performed using the Origin software.

believe that the fact that the alignment is better for the less concentrated azo-dye polymer films is probably related to the free volume for reorientation of the photochromic side chains in the polymeric matrix. No photoalignment effect was observed in the NLC molecules, for the polymer film containing 6% of azo-dye groups which indicates that there must be a minimum concentration of chromophores to get a macroscopical effect. The orientation of the NLC induced by photoalignment remains for a long period (at least for 7 months) however, a new orientation can be recorded by irradiating the cell with a different polarization direction. The photoalignment presents a good thermal stability which is an important feature for technological applications.

The experiments performed have shown that the photoalignment does not induce a pretilt angle on the NLC molecules, which means that the reorientation of the director consists essentially of a rotation in the plane parallel to the boundary surface. This is consistent with the fact that no significative change in the zenithal anchoring strength is observed when the cell is submitted to the photoalignment. Nevertheless, the final director orientation depends on the chromophores concentration and on the incident energy. The azimuthal anchoring strength can be varied two orders of magnitude, $10^{-8} - 10^{-6}$ J/m², by choosing properly the concentration of chromophores and the incident energy. This is an important aspect because it allows the manipulation of two parameters to control the anchoring strength in NLC cells. The experimental results show that doubling the azo-dye concentration from 17% to 38%, the corresponding azimuthal anchoring strength values W_ϕ are almost the same. However, when a concentration of 60% is used, a significative change in W_ϕ resulted. This observation indicates that

there is no linear relationship between the azo-dye concentration and the anchoring strength.

In a previous work [22], we have irradiated a polymer film with 60% of chromophores with an incident power $\sim 10^2$ lower than used in the experiments described here and we observed that the photoalignment induced to the liquid crystal cell, reached also a saturation level. The maximum anchoring energy determined then, was 5×10^{-6} J/m², which is in good accordance with the maximum value reported here, for the same chromophores concentration, however, in the previous experiment the photoalignment was not stable. For polymeric films containing azo-dye groups it has been reported a dependence of reorientation on the irradiation intensity, which is a characteristic of a collective process [23].

In our measurements, the observed reorientation on the LC molecules is due to the reorientation of the azo-dye groups in the polymer film and to the coupling of LC molecules to the polymer film. This indicates that besides the collective reorientation of the azo-dye groups, which depends on intensity, there is a complex interaction between the polymer film and the LC that depends on the population of oriented chromophores. A theoretical description that allows us to get a relation between the chromophores concentration in a particular configuration and the induced orientation to the NLC molecules is still lacking. A detailed study concerning the dynamics of the photoalignment process is in course, that could help for a better understanding of more fundamental aspects related to this process.

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