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Liquid Crystal Photoalignment on Azo-Dye Layers

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Effective photoalignment of liquid crystals (LCs) on spin-coated layers of azo dyes on the surface of ITO was observed. Methyl Red films were irradiated with linearly polarized light from an Ar^+- laser. The layers align the easy orientation axis of LC 5CB perpendicular to the polarization of the incident light. Photo-induced cis/trans isomerization and changes of the interaction between dye molecules and the surface of the ITO are the proposed mechanism of photoalignment. Photoalignment of 5CB on layers of sulfasalazine after exposure to polarized UV light was also explored. A thermal induced anchoring transition was observed in addition to features similar to those of methyl red.

Keywords: liquid crystal; photoalignment; methyl red; sulfasalazine

INTRODUCTION

Uniform alignment of liquid crystals (LC) is of great importance for liquid crystal displays. Of all the methods available to achieve surface induced alignment, linearly polarized light irradiation has proved to have many advantages. Most of the studies in this area have focused on light-induced anisotropy of polymer films, using different types

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of cinnamates[1-4], polyimides,[5,6] polymer films with photosensitive main chain[7] or side chains,[8] and dye-doped polymer films.[9] Dyes chemically bonded to the substrate have also been investigated.[10,11] Here we report on the first observations of photoalignment of LC by azo-dye layers spin-coated onto ITO glass. The dyes used were Methyl Red (MR) and Sulfasalazine (SA).

EXPERIMENTAL

The chemical structures of methyl red and sulfasalazine are shown in Figure 1. MR and SA were first dissolved in isopropanol (*i*-PrOH), then spin-coated onto ITO substrates to produce films of different thickness. Solution of higher concentration gives thicker film because the rest of the spin-coating conditions are the same for all the films. As shown in Table 1, films of different thickness are indicated by the concentration of the corresponding original solutions.

TABLE 1. Methyl red films obtained from solutions of different concentration.

Film	A	B	C
Concentration of IPA solution(wt%)	0.05	0.01	0.005

Azimuthal alignment of nematic liquid crystal was obtained by irradiation with linearly polarized Ar+ laser light (Ion Laser Technology) and UV light (Oriel model 6266) for MR layers and SA layers, respectively. For MR the 501nm line of the Ar+ laser was used. For SA, the light source was a Xe lamp. The UV-vis spectra of the tested films were measured using an UV-visible spectrometer (Perkin-Elmer Lambda 19.22). The alignment of LC was tested in combined LC cells made from reference and tested surfaces, as shown in Figure 2. The thickness of the cell is 47 micron. The reference surface was covered with a rubbed polyimide layer providing strong anchoring with a fixed planar easy axis. The tested surface was made from the studied materials. The aligning polyimide surface determined the preferred planar orientation of LC in the cell parallel to the rubbing direction. After irradiation of the spin-coated dye layers, the cells were

assembled and then filled with the liquid crystal 5CB (K15 from Merck) in the isotropic state (50°C) for irradiated MR layers, and in both nematic state at room temperature (20°C) and isotropic state (50°C) for SA layers. The angle between the director on the tested surface and the easy axis of the rubbed PI, φ, was measured using a polarizing microscope.

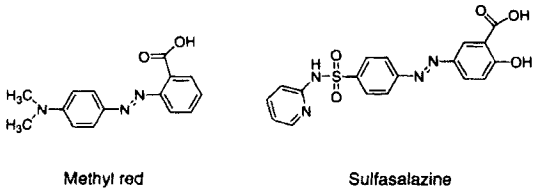

FIGURE 1. The structures of methyl red and sulfasalazine

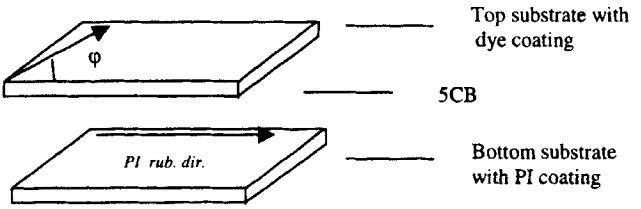

FIGURE 2. Fabrication of the cell

RESULTS AND DISCUSSION

In all cases, the light exposure resulted in a twisted planar LC orientation in the illuminated area, which was stable in time and at room temperature. As shown in Figure 3, no observable alignment was shown for irradiation time under 1 minute. Then the angle φ increased rapidly for short exposure time, t_{exp}, then remained constant with further exposure after reaching the maximum value φ ≈45°. This behavior indicates that the light irradiation produces the easy axis

perpendicular to the polarization of light, ***E***. The increase of the angle φ at the beginning of the exposure, $\varphi(t_{exp})$, is produced by the increase of the anchoring energy, *W*, which is associated with the light-induced easy axis. The achievement of the value of $\varphi \approx 45^{\circ}$ for cells with dye films of different thickness means that a strong anchoring ($W \geq K/L$) is realized on the tested surface [12]. In our case the value of the Frank constant is $K = 4*10^{-7}$ dyne and we can estimate that the light-induced anchoring energy reaches the value of $W \geq 10^{-2}$ erg/cm^2.

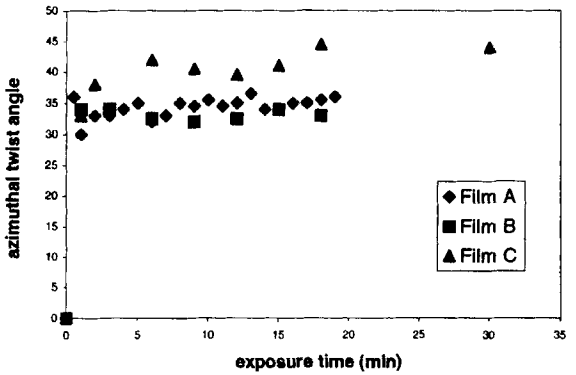

FIGURE 3. Dependence of φ with exposure time for methyl red . Film thickness: A>B>C. (Ar^+ laser output power: 3*mW*)

The nature of the observed effect deserves further studies. We speculate that the underlying mechanism of the effect is rearrangement of the MR layer as the most probable origin of photoalignment effect.

Polarized light exposure can modify the initial isotropic angular distribution of the adsorbed molecules. Indeed, the methyl red molecule is strongly dichroic, which results in the angular selective absorption in the MR layer. Depending on the mechanisms of the light action, the following ordering processes could be expected:

Photo-induced transformation of MR molecules. For example, light-induced decomposition of MR molecules should result in anisotropic angular distributions for both unreacted molecules and photo-transformed molecules. These irreversible reactions will produce an anchoring energy expected to reach a maximum and then decrease. Reversible cis/trans isomerization of MR

molecules will also result in an anisotropic distribution, and the anchoring energy will be expected to approach a constant maximum value.

Photo-induced changes of the MR – ITO surface interaction. It is reasonable to suggest that the excitation of MR molecules can provoke drastic changes to their interaction with ITO surface, resulting in a new stable state of LC molecules on the ITO surface. For example, it is possible to presume appearance or disappearance of the H-bonds between MR molecules and OH-groups from the ITO surface.

Light-induced desorption. Absorption dichroism of MR molecules could lead to anisotropic desorption of molecules from the surface. It results in anisotropy of the MR layer.

Light-induced reorientation of the MR molecules perpendicular to the polarization of the incident light. The effects of the molecular reorientation perpendicular to the vector ***E*** are well known. The studies of azo-polymer have shown such effect. [13-15] Ichimura et al.[16,17] found in-plane reorientation of LC on a quartz surface modified with azobenzene and cinnamic units. These effects are explained by the consequent trans-cis-trans-cis-... isomerization of photosensitive fragments perpendicular to the vector ***E***. This model includes a sharp increase in the rotation mobility of the photosensitive fragments during trans-cis isomerization and strong positive dichroism of trans-isomers. The increase of the rotation mobility leads to changes of the fragment orientation during trans-cis isomerization. If a photosensitive fragment is oriented perpendicular to the vector ***E***, it is trapped because it does not absorb light in this orientation. Therefore, the molecular angular distribution is enriched with the molecules oriented perpendicular to ***E***. As shown in Figure 3, we did not see any decrease of the light-induced twist angle φ after its achievment of the maximum value. This allows us to rule out these two mechanisms: light-induced desorption and irreversible phototransformation of MR molecules. The mechanisms left are trans-cis isomerization, changes of the MR – ITO surface interaction and reorientation of MR molecules perpendicular to the vector ***E***.

The actual mechnism was deducted from and supported by the data of the spectral studies. The changes in the absorption spectrum

MR films with exposure time are shown in Figure 4. Figure 5 gives the change of absorbance at λ_{max} with the exposure time.

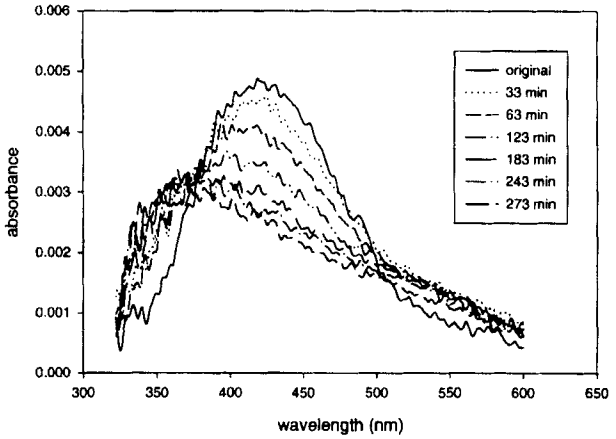

FIGURE 4. Change of absorption spectrum with exposure time for methyl red.

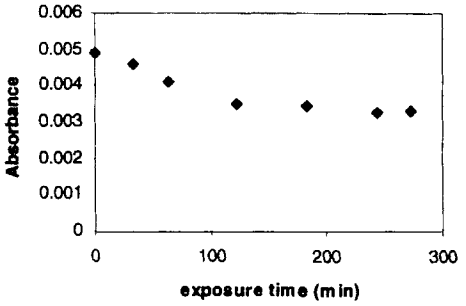

FIGURE 5. Change of absorbance at λmax with exposure time for methyl red.

The absorbance first decreases rapidly, then changes very little with the exposure time, approaching a steady state. This behavior is typical for trans/cis isomerization of azo-dyes. [18] The cis-isomer absorbs to the blue of trans-isomer. Therefore, the excitation of cis-isomers results in the broadening of the blue wing of the adsorption band. The isomerization is a reversible reaction and the absorption bands of trans- and cis- isomers overlap. Hence, the equilibrium point can be reached after a suitable exposure dose. The steady state seen in Figure 5 is this equilibrium point. The evident changes of the shape of the absorption band after the irradiation makes the mechanism of light-induced reorientation of MR molecules seems unlikely. Thus, we are left with the trans-cis isomerization and changes of the MR–ITO surface interaction.

The interaction between MR-molecules and ITO surface is rather strong and easy to observe in the absorption spectra. As illustrated in Figure 6, the evident shift of absorption peak to the lower wavelength and changes of the shape of the absorption band with the decrease of the film thickness can be attributed to two possible processes. The changes in the shape and position of absorption band may be caused by the appearance of hydrogen bonds between MR

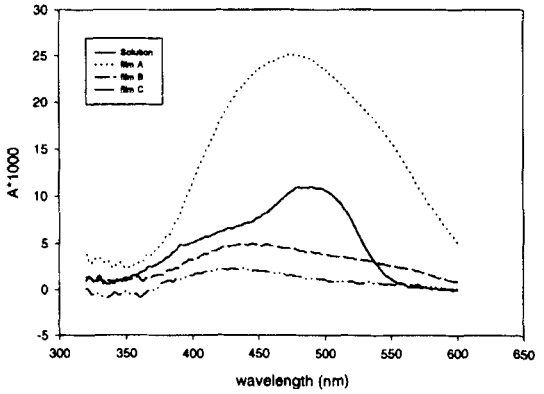

FIGURE 6. Absorption spectra for methyl red films and methyl red in isopropanol solution.

molecules and hydroxyl groups on the ITO surface. Or it can be caused by an increase in the proportion of the cis isomer at the ITO surface due to the interaction of MR molecules with the surface. The second effect may also be related to the first one.

Thus, at the present state of our knowledge, the mechanism of photoalignment of LC by MR films can be described as the following: The adsorbed MR molecules have strong interaction with the ITO surface. The absorption of light causes isomerization of the molecules and, in turn, changes their interaction with the ITO surface. Both factors result in changes of interaction of MR molecules with molecules of LC. Because of adsorption dichroism of MR molecules, the angular distribution of phototransformed MR molecules is anisotropic. It leads to the anisotropic angular interaction of the director of LC with the MR films and thus to the appearance of the easy axis.

Besides the study on the photoaligning properties of MR, we carried out tentative studies of photoalignment of 5CB by spin-coated layers of sulfasalazine irradiated with polarized UV light. We found that the direction of LC alignment strongly depends on the filling state of liquid crystal. The easy axis is perpendicular to the polarization of UV light when the cell is filled with LC in nematic phase ($T = 20^{\circ}C$). However, when filled under isotropic phase ($T = 50^{\circ}C$), the easy axis is parallel to the polarization of UV light. Heating of the cell that is filled under nematic phase causes reorientation of LC parallel to the polarization of UV light. The nature of this anchoring transition requires further investigations.

CONCLUSIONS

Photoalignment of liquid crystals by azo dye layers spin coated on ITO glass substrates after exposure to linearly polarized light was observed. Both methyl red and sulfasalazine produce good alignment. Photo-induced cis/trans isomerization and changes of the interaction between MR molecules and the surface of ITO are proposed to be the mechanism of the photoalignment effect of methyl red. Further experiments are in progress for the anchoring transition process of sulfasalazine.

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References

[1] A. Dyadyusha, V. Kozenkov, T. Marusii, Yu. Reznikov, V. Reshetnyak and A. Khizhnyak, *Ukr. Fiz. Zh.* **36,** 1059 (1991) (in Russian).
[2] M. Schadt, K. Schmitt, V, Kozenkov, and V. Chigrinov, *Jpn. J. Appl. Phys.* **31,** 2155 (1992).
[3] T. Marusii and Yu. Reznikov, *Mol. Mater.* **3,** 1614 (1993).
[4] A.G. Dyadyusha et al. *Mol. Cryst. Liq. Cryst.* **263**, 339 (1995).
[5] J. Chen, D.L. Johnson, P.J. Bos, X. Wang, J. West, *Phys. Rev. E* **54**(2), p. 1599 (1996).
[6] M. Nishikawa, B. Taheri, and J.L. West, *Appl. Phys. Lett,* **72,** 2403 (1998).
[7] S. Song et al., *Jpn. J. Appl. Phys.*Pt 1, **37,** 2620, (1998).
[8] S. Fumuri, M. Nakagawa, S. Morino, K. Ichimura and H. Ogasawara *Appl. Phys. Lett,* **74,** 2438 (1999).
[9] W. Gibbons, P. Shannon, Shao-Tang Sun and B. Swetlin, *Nature* **351,** 49 (1991).
[10] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki, *Langmuir* **4,** 1214 (1988).
[11] K. Ichimura, T. Seki, Y. Kawanishi, Y. Suzuki, M. Sakuragi, T. Tamaki. *Photo-reactive Materials for Ultrahigh Density Optical Memory,*Elsevier, Amsterdam, 55–83 (1994).
[12] D. Voloshchenko, A. Khizhnyak, Yu. Reznikov, V. Reshetnyak, *Jpn. J. Appl. Phys.* **34,** 566 (1995).
[13] M. Dumont, G. Froc, S. Hosotte, *Nonlinear Optics,* **9,** 327 (1995).
[14] S. Palto, G. Durand. *J. Phys. II* **5** (7) 963–978, (1995).
[15] A. Tereshchenko, L. Shanski, O. Yaroshchuk, J. Lindau. *Optics and Spectroscopy,* **83**(5), 747 (1997).
[16] K. Ichimura et al. *Appl. Phys. Lett.* **63**(4), 449–451 (1993).
[17] H. Tomita, et al. *Liquid Crystals* **20** (2) 171–176 (1996).
[18] D. C. Neckers: *Mechanistic Organic Photochemistry* (Reinhold, New York, 1967) pp. 203–207.