

27.1: Invited Paper: New Developments in Liquid Crystal Photo-Aligning by Azo-Dyes

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Abstract

Liquid crystal photo-alignment using azo-dyes is reviewed. This alignment method is very different from previously reported ones, such as photo-crosslinking, photo degradation and photo-isomerization. It will be shown that this photo-aligning method can provide a controllable pretilt angle and strong anchoring energy of the liquid crystal cell, as well as high thermal and UV stability. The application of this method to the alignment and fabrication of various types of liquid crystal displays is also discussed.

1. Introduction

The field of liquid crystal (LC) photo-alignment is very rapidly developing and a vast amount of the new materials, techniques and LCD prototypes based on photo-alignment (PA) technology have appeared recently [1-9]. However, despite these potential advantages, the application of PA to LCD production is still limited to the laboratory. Large scale deployment of PA is hampered by the lack of a good material and by long term stability, not to mention the lack of suitable mass production scale equipment. The effect of LC photoalignment is a direct consequence of the appearance of the photo-induced optical anisotropy and dichroic absorption in thin amorphous films, formed by molecular units with anisotropic absorption properties [1]. The first publication on LC photo-alignment appeared in 1988, which discussed the application of a reversible cis-trans isomerization of the azo-benzene molecular layers [2]. The optical control of LC alignment was made by changing the wavelength of the non-polarized light illumination [2]. Later it was shown that the alignment of a liquid crystal medium could be made by illuminating a dye doped polymer alignment layer with polarized light [3]. LC molecules in contact with the illuminated area were homogeneously aligned perpendicular to the direction of the laser polarization and remained aligned in the absence of the laser light. Subsequently, LC photo-alignment was also achieved using cinnamoyl side-chain polymers [4,5] and polyimide aligning agents [6]. More recently, a new class of azo-dyes have also been studied with excellent results [10,11]. In this paper, we shall review the physical mechanism of this alignment process and report some new results related to the processing conditions using these azo-dyes. In particular, we discuss the conditions where the light dosage is greatly reduced, to less than 50mJ/cm². Applications of this new PA material to various types of LCD will also be reviewed.

2. Results

2.1 Azo-dye aligning layers

Photo-alignment can generally be classified into four categories according to their mechanism. They are (i) photochemically reversible cis-trans isomerization in azo-dye containing polymers, monolayers and pure dye films [12,13]; (ii) photochemical crosslinking in preferred directions of polymer precursors, such as cinnamoyl side-chain polymers [4,5]; (iii) photodegradation and orientational bond breaking in polyimide materials [14,15]; and (iv) pure reorientation of the azo-dye chromophore molecules or azo-dye molecular solvates due to the diffusion under the action of polarized light [10,11]. Recently the method of repeated cis-trans photoisomerization reaction resulting in the reorientation of the backbone structure of polyamic acid contained azobenzene units was reported [16,17]. We believe that the method (iv) with pure diffusion reorientation of the azo-dye chromophore molecules or azo-dye molecular solvates is the most promising one for large scale applications. In this case the azo-dye molecules, are tending to align their long axes perpendicular to the UV-light polarization resulting in anisotropic dichroism or birefringence of the PA film [18]. Actually the photo-aligned azo-dye molecules produce a very smooth and uniform structure with the thickness of several nanometers controlled by the concentration of the azo-dye in an organic solvent e.g. N,N-dimethylformamide (DMF) [11]. The change of the azo-dye concentration between 0.4 and 1.3 wt/wt % concentration results in the thickness variation of the photo-alignment layer between 3 and 12 nm [19]. The order parameter S of a sulphuric azo-dye SD1 measured from the absorption spectra is equal to -0.4 at $\lambda_m = 372$ nm (absorption maximum), which is 80% from its maximum absolute value $S_m = -0.5$ in our case.

In order to improve the durability against light exposure and moisture, the polymerization of the azo dyes after the photoalignment was investigated, synthesizing azo dye monomer SDA1 [11]. It was dissolved in DMF and doped by 0.02 % of a thermal polymerization initiator V-65 (form Wako Pure Chemicals Industries, Ltd.). The mixture was spin-coated onto glass substrates and photoaligned in the same manner as SD1. After the photoalignment, the SDA1 film was heated at 150°C during 1 hour for the purpose of thermal polymerization. LC on the SDA1 film was aligned in the same direction as SD1. LC alignment properties of the polymerized azo-dye layer were thermostable up to 250°C, while SD-1 has degraded at this temperature. Improvement of durability against UV light exposure in the LC cell using SDA1 photo-aligned film after the thermal polymerization was also confirmed. The dose of UV-

light of 175 MJ/m^2 can be tolerated by SDA-1 layer, while SD-1 layer is destroyed by this UV light dosage. Later the new more stable photo-polymerized azo-dye called SDA-2 was synthesized [11].

Usually the azimuthal anchoring energy of photo-aligning materials is rather small (about $1\text{--}7 \times 10^{-6} \text{ J/m}^2$), which is about an order of magnitude smaller than the value obtained by the rubbing method [20-24]. A perfect quality homogeneous alignment was obtained on polyimide films, but a relatively high energy of illumination ($\approx 7 \text{ J/cm}^2$) was needed to get the required maximum order parameter [7]. We studied the LC aligning properties of the azo-dyes. The temperature stable pretilt angle of 5.3° was obtained by a two-step exposure of azo-dye film using normally incident polarized light followed by oblique non-polarized light. The pretilt angle was temperature stable and does not change after heating the sample up to 100°C for two hours. The azimuthal anchoring energy W_ϕ of a photo-aligned substrate was measured [23]. It was found that the anchoring energy was very high and $> 10^{-4} \text{ J/m}^2$, which is the same as the anchoring of the rubbed polyimide (PI) layer. As a comparison, in photo-polymerized azo-dye layers, the azimuthal and polar anchoring energies were about $1.5 \cdot 10^{-5} \text{ J/m}^2$ and $3 \cdot 10^{-4} \text{ J/m}^2$ for the exposure dose less than 1 J/cm^2 . The value of voltage holding ratio (VHR) was also measured. The measured values for the photo-aligned LC cell ($>99\%$ at 80°C) and residual DC voltage ($<50\text{mV}$) was found to be even better than those for rubbed PI layers.

We have also demonstrated that a super-thin photo-aligned layer azo-dye layer can be used for LC photo-aligning. This new method includes the formation of a very neat “textile knitwear” by a super-thin SD-1 layer and allows to avoid the spin-coating procedure. Moreover, the photosensitivity of azo-dye after photo-alignment can be further reduced and “island” azo-dye structure onto the rough ITO surface can be prevented due to better adhesion of SD-1 molecules. Using this super-thin SD-1 layer as an alignment agent, the sufficiently high polar and azimuthal anchoring energy and a perfect LC alignment can be obtained [25]. The method allows to get a perfect LC photo-alignment in large or curved cells and is very attractive for mass production.

We also examined the effect of light intensity on the PA process. Recently we have synthesized certain azo-dye derivatives, which considerably improve the sensitivity of SD-1, so very low dosage of UV-light is sufficient for a perfect uniform alignment of LC cell: 150 mJ/cm^2 for a non-polarized light and 20 mJ/cm^2 for a polarized light [26].

2.2 Applications

A remarkable property of azo-dye aligning layers gives a good chance to provide a high photoalignment quality of *ferroelectric liquid crystal* (FLC) using the azo-dye layer. The photo-aligned FLC cell appeared to be better than prepared by buffing, if the UV-irradiation time of the azo-dye layer is high enough [27]. The FLC row addressing response time of $\tau \approx 100 \mu\text{s}$ at the voltage pulse amplitude of $U = \pm 15\text{V}$ was demonstrated [27, 28]. Large FLC cell gaps of $5 \mu\text{m}$ and $7 \mu\text{m}$ were used, which is easy in manufacturing. Perfect electrooptical performance of the photo-aligned FLC display with a memorized gray scale was demonstrated. A prototype of passively addressed passive matrix

FLC display based on the photo-alignment technique was developed [28]. Recently photoaligned bistable FLC with dichromatic (two color) [29] and almost achromatic (black/white) [30] switching were realized. 160×160 passive matrix addressed bistable $5 \mu\text{m}$ FLC display was demonstrated with the driving voltage of $\pm 13\text{V}$ and $5 \mu\text{m}$ cell gap [31]. Images can be saved for very long time without any power supply.

VAN-LCD has become very popular for LCD TV applications because of the high contrast and wide viewing angle it affords. In experiment [32] the commercially available polyimide (PI) for homeotropic alignment was used in a combination with azo-dye for varying the pretilt angle from the homeotropic direction. The composition of 1% of azo-dye in solution with PI was prepared and the photo-aligning films were illuminated by a slantwise nonpolarized light. For comparison the aligning film of a pure PI was prepared by rubbing technique to align the LC molecules in a homeotropic state with some pretilt angle. The measured value of the pretilt angle from the homeotropic alignment was about 1.4° , which is higher than in other photo-aligned VAN LC cell (0.53°). Later the pretilt angles of $2\text{--}3^\circ$ from the homeotropic LC orientation were obtained using the mixture of homeotropic PI and photopolymerized azo-dye SDA-2 [11]. The measured value of the contrast ratio between “off” and “on” states in all the cases exceeds 1000:1 in the monochromatic light. Thus it is concluded that azo-dyes are suitable for the alignment of VA-LCD.

We fabricated *truly bistable π -BTN* display, based on photoaligning technology [33]. The strong anchoring surface was achieved by the usual rubbed polyimide (PI) layer. Such PI layer provides a strong polar anchoring energy of $1.5 \times 10^{-3} \text{ J/m}^2$. We found that the polar anchoring energy of photo-polymerized azo-dye SDA-1 (SDA-2) can be adjusted to $1.5\text{--}2.8 \cdot 10^{-4} \text{ J/m}^2$, while azimuthal anchoring to $3.6\text{--}5.6 \cdot 10^{-5} \text{ J/m}^2$ by changing the exposure time, which was suitable for obtaining π -BTN bistability by surface anchoring breaking. The π -BTN LCD was switched between -22.5° and 157.5° , exhibiting a high contrast ratio ($\text{CR} > 140$) and wide viewing angles [33]. π -BTN was also successfully made on flexible plastic substrates using photo-alignment technology [34]. This facilitates the implementation of low-power consumption bistable liquid crystal display into smart cards [34].

We have also investigated the properties of *azo-dye alignment on plastic substrates* [35]. Excellent alignment with a high anchoring energy was achieved with the exposure energy less than 1.0 J/cm^2 , which corresponds to the azimuthal anchoring energy $> 10^{-4} \text{ J/m}^2$. We used a mixture of azo-dye SD-1 with a mentioned above thermo-polymerized azo-dye SDA-2 for the display fabrication. The LC pretilt angle of about 5° on the plastic substrate was made by a double exposure method. To demonstrate the alignment quality on plastic substrates a 9-digit reflective passive matrix TN-LCD mounted in smart card was fabricated. To maintain a uniform cell gap of $8 \mu\text{m}$ (second Mauguin minimum of MLC-6809-000 Merck LC mixture), semi-dry adhesive spacers were chosen. The electrooptical performance of the photo-aligned plastic display was very similar to common TN-LCD fabricated for comparison by usual rubbing method on glass substrate.

We propose an optically rewritable twisted nematic liquid crystal display (TN-LCD), based on photoaligning technology [36]. TN-LCD does not require an electronic scheme, a power supplier, conductive layers inside devices, which provides a possibility to use this type display in plastic cards, registration and other systems. An optically rewriteable LC display shows a high contrast and a long life time. We propose to use TN-LCD cell with special alignment layers and without conductive layers. In our display we change LC orientation on the alignment layer by a polarized light. The similar devices in twist LCD cell with light controllable azimuthal anchoring energy were first reported by Yamaguchi et al. [37,38]. Our photosensitive azo-dye material SD-1 reversibly change the orientation in the plane of the substrate, while the other substrate keeps a strong azimuthal anchoring energy. It gives a possibility to change the twist angle in LC cell. For a dark state we use the structure with a zero twist angle and for a bright state –the structure with the twist angle close to 90° between two crossed polarizers and apply a special mask to create the image. Any gray level can be realized in such an image, as azimuthal anchoring energy and consequently the apparent twist angle are proportional to the intensity of UV light passed through the mask [36]. As azo-dye SD-1 can change its alignment reversibly without any photochemical transformations and photo-chemical reactions, our procedure will allow us to erase and write images an unlimited number of times. As the sensitivity of new SD-1 modifications for a polarized light is about $20\text{mJ}/\text{cm}^2$ [26] for a polarized light the usual UV lamp with a polarizer can erase and write the image in several seconds. The image can be kept for infinitely long time, provided, that UV polarized light of 365 nm is avoided and can be readable only, if a polarizer is used. The latter is quite reasonable for such application, as plastic displays for credit cards.

We have developed a photo-alignment technology for liquid-crystal-on silicon (LCOS) microdisplays [39]. Three step exposure process was proposed to improve the quality of LC tilted alignment on the photo-aligned surface. Both azimuthal and polar anchoring energies on the photoaligned surfaces were high and comparable to those of rubbed polyimide layers. Consequently, photo-aligned LCOS panels have the same electrooptical characteristics as usual ones prepared by rubbing. A high contrast and fast response were demonstrated, which meet microdisplay standards. It was also observed, that defects were greatly reduced in photo-aligned LCOS microdisplays due to the non-contact nature of photoaligning technology.

3. Conclusion

In this paper we have briefly reviewed a new photo-aligning technology based on photo-induced reorientation of dye molecules. We have shown that basic optical studies are consistent with the notion that the dye molecules reorient themselves in the potential field generated by the light and are held in place by their intermolecular potentials. We have also pointed out that the processing condition can be quite important, with a minimum sensitivity of $20\text{mJ}/\text{cm}^2$ possible under the best conditions. This is highly desirable for manufacturing. As well, we considered the temperature and UV-stability of such LC photo-alignment with a sufficiently high pretilt angle. The possibility to use this new photo-aligning layer for FLC, VAN-LCD, π -BTN LCD, optical rewritable memory, microdisplays, and TN-LCD on plastic substrates has been also demonstrated.

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5. References

- [1] E. Kvasnikov, V. Kozenkov, , and V. Barachevskii, *Dokladi Akademii Nauk SSSR*, **237**, 633 (1977) (In Russian).
- [2] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki, and K. Aoki, *Langmuir*, **4**, 1214 (1988).
- [3] W. Gibbons, P. Shannon, S. Sun, and B. Swetlin, *Nature*, **351**, 49 (1991).
- [4] M. Schadt, K., Schmitt, V. Kozenkov, and V. Chigrinov, *Jpn. J. Appl. Phys.*, **31**, 2155 (1992).
- [5] A. Dyadyusha, T. Marusii, Yu. Reznikov, A. Khizhnyak, and V. Reshetnyak, *JETP Lett.*, **56**, 17 (1992) (In Russian).
- [6] M. Hasegawa, and Y. Taira, *IDRC '95 Digest.*, p.213.
- [7] M. O'Neill, and S. Kelly, *J. Phys. D.*, **33**, R67 (2000).
- [8] M. Schadt, *Mol. Cryst. Liq. Cryst.*, **364**, 151(2001).
- [9] V. Chigrinov, V. Kozenkov, and H.S. Kwok, In a book "Optical Applications of Liquid Crystals", Ed. by L. Vicari, Institute of Physics Publishing, Bristol and Philadelphia, pp.201-244, 2003.
- [10] V. Chigrinov, E. Prudnikova, V. Kozenkov, H.S. Kwok, H. Akiyama, H. Kawara, H. Takada, H. Takatsu, *Liq. Cryst.*, **29**, 1321 (2002).
- [11] H. Takada, H. Akiyama, H. Takatsu, V. Chigrinov, E. Prudnikova, V. Kozenkov, H.S. Kwok, *SID '03 Digest*, p.620.
- [12] T. Pedersen, P. Ramanujam, P. Johansen, S. Hvilsted, *J. Opt. Soc. Amer.*, **15**, 2721 (1998).
- [13] D. Statman, and I. Janossy, *J. Phys. Chem.*, **118**, 3222 (2003).
- [14] M. Nishikawa, B. Taheri, B., and J. West, *Appl. Phys. Lett.*, **72**, 2403 (1998).
- [15] S. Gong, J. Kanicki, L. Ma, and J. Zhong, *Jpn. J. Appl. Phys.*, **38**, 5996 (1999).
- [16] B. Park, Y. Jung, H.-H. Choi, H.-K. Hwang, Y. Kim, S. Lee, S.-H. Jang, M. Kakimoto and H. Takezoe, *Jpn. J. Appl. Phys.*, **37**, 5663 (1998).
- [17] K. Sakamoto, K. Usami, M. Kikegawa, M., and S. Ushioda, *J. Appl. Phys.*, **93**, 1039 (2003).
- [18] V. Chigrinov, S. Pikin, A. Verevochnikov, V. Kozenkov, M. Khazimullin, J. Ho, D. Huang, and H.S. Kwok, *Phys. Rev. E*, **69**, pp.061713 (2004).
- [19] E. Pozhidaev, V. Chigrinov, D. Huang, A. Zhukov, J. Ho, and H.S. Kwok, *Jpn. J. Appl. Phys.*, **43**, 5440 (2004).
- [20] S.-K. Hahn, and D. Kang, *IMID '03 Digest*, p.619.
- [21] L.T. Thieghi, R. Barberi, J. Bonvent, E. Oliviera, J. Giacometti, and D. Balogh, *Phys. Rev. E*, **67**, 041701 (2003).
- [22] X. Lu, Q. Lu, and Z. Zhu, *Liq. Cryst.*, **30**, 985 (2003).
- [23] V. Chigrinov, A. Muravski, H.-S. Kwok, H. Takada, H. Akiyama, and H. Takatsu, *Phys. Rev. E*, **68**, 061702 (2003).
- [24] V. Kozenkov, V. Chigrinov, and H.-S. Kwok, *Mol. Cryst. Liq. Cryst.*, **409**, 251 (2004).
- [25] X. Li, V. M. Kozenkov, F. Yeung, P. Xu, V. Chigrinov, and H. S. Kwok, *Jpn. J. Appl. Phys.*, **45**, 203 (2006).
- [26] H.S. Kwok, V. Chigrinov, H. Takada, H. Takatsu, *IEEE/OSA J. of Disp. Techn.*, **1**, 41(2005).
- [27] D. Huang, E. Pozhidaev, V. Chigrinov, H. Cheung, J. Ho, and H.S. Kwok, *Displays*, **25**, 21(2004).

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- [28] D. Huang, E. Pozhidaev, V. Chigrinov, H. Cheung, J. Ho, and H.S. Kwok *J. of SID*, **12**, 455 (2004).
- [29] I. Valyukh, S. Valyukh, K. Skarp, V. Chigrinov, *EuroDisplay 2005 Digest*, p. 305.
- [30] P. Xu, X. Li, and V. Chigrinov, *Jpn. J. Appl. Phys.*, **45**, 200 (2006).
- [31] X. Li, A. Murauski, A. Murauski, H. L. Cheng, P. Xu, E. Pozhidaev, and V. Chigrinov, *SID'06 Abstracts*, P.232L, San Francisco, June, 2006.
- [32] V. Konovalov, V. Chigrinov, H.S. Kwok, H. Takada, and H. Takatsu, *Jpn. J. Appl. Phys.*, **43**, 261(2004).
- [33] F. Yeung, and H.S. Kwok, *Appl. Phys. Lett.*, **83**, 4291 (2003).
- [34] X. Li, F. Yeung, V. Chigrinov, and H.S. Kwok, *IDW'05 Digest*, p.883.
- [35] J. Osterman, A. Tong, K. Skarp, V. Chigrinov, and H.S. Kwok, *J. of SID*, **13**, 1 (2005).
- [36] A. Murauski, V. Chigrinov, X. Li, and H.S. Kwok, *IDW'05 Digest*, p.131.
- [37] R. Yamaguchi, Y. Goto, Y., and S. Sato, *Jpn. J. Appl. Phys.*, **41**, L889 (2002).
- [38] R. Yamaguchi, T., Kawamura, and S. Sato, S., *IDW'04 Digest*, p. 39.
- [39] B. Zhang, B., K. Li, V. Chigrinov, H.S. Kwok, and H.C. Huang, *Jpn. J. Appl. Phys.*, **44**, 3983 (2005).