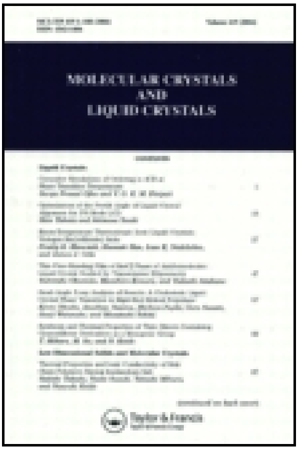

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Generation of Pretilt Angles on Polyimides with a Single Linearly Polarized UV Exposure

Michinori Nishikawa [a b] & John L. West [a]

[a] Kent State University, Liquid Crystal Institute, Kent, Ohio, 44242, USA

[b] JSR Co., Yokkaichi Research Laboratories, 100, Kawajiri-cho, Yokkaichi, Mie, 510-8552, Japan

Version of record first published: 24 Sep 2006

To cite this article: Michinori Nishikawa & John L. West (1999): Generation of Pretilt Angles on Polyimides with a Single Linearly Polarized UV Exposure, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 329:1, 579-587

To link to this article: http://dx.doi.org/10.1080/10587259908025984

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 579-587
Reprints available directly from the publisher
Photocopying permitted by license only

Generation of Pretilt Angles on Polyimides with a Single Linearly Polarized UV Exposure

MICHINORI NISHIKAWA[ab] and JOHN L. WEST[a]

[a]*Kent State University, Liquid Crystal Institute, Kent, Ohio, 44242, USA and*
[b]*JSR Co., Yokkaichi Research Laboratories, 100, Kawajiri-cho, Yokkaichi, Mie, 510–8552, Japan*

We designed polyimide (PI) films containing fluorine atoms for liquid crystal (LC) alignment using linearly polarized UV exposure. Using a single oblique polarized UV exposure we obtained unidirectional LC alignment with any desired pretilt angles from 0 ° up to 90 °. Pretilt angles depend on the concentration of fluorine atoms in PI and the UV exposure time and angle. Dichroic ratio and capacitance measurements of the LC cells suggest that oblique polarized UV exposure breaks the surface order degeneracy of the LC molecules, generating uniform pretilt angle along the optic axis of PI film.

Keywords: liquid crystal; polyimide; pretilt angle; polarized UV exposure

INTRODUCTION

Liquid crystal (LC) alignment using polarized UV exposure[1] is a promising candidate for overcoming problems such as generation of static charge, dust, or scratches caused by rubbing. However, generation of pretilt angle using this technique is not easy because conventional photo-alignment materials, poly(vinyl cinnamate)[2] and polyimides (PIs)[3,4], result in LC alignment perpendicular to the UV polarization. Some methods have been proposed to generate pretilt angles: (1) double polarized UV exposure with different polarization and irradiation angles[5], (2) combined polarized UV exposure with both p-wave and s-wave[6], (3) oblique polarized UV exposure on poly(coumarin)[7]. Double UV exposure is too complicated for mass production, and combined UV exposure with both p- and s-wave decreases the polarization efficiency of the polarizer. Poly(coumarin) aligns the LC parallel to the polarized UV direction and results in any desired pretilt angle by adjusting the oblique irradiation angle. However, the long term reliability of the LC displays incorporating UV cured poly(coumarin) alignment film is uncertain because of the unreacted coumarin group and lower glass transition temperature.

In our previous papers, we have reported that PI materials containing fluorene units align LC parallel to the UV polarization[8] and the introduction of fluorine atoms into PI[9] generates any desired pretilt angles from 0 ° up to 90 °. However, the mechanism of generation of pretilt angles has not been clarified. In this paper, we explore the mechanism of generation of pretilt angles on PIs with a single oblique linearly polarized UV exposure.

EXPERIMENTS

PI materials used in these experiments are shown in Fig. 1. These PI films photo-decompose upon UV exposure[8]. PI films were prepared by heat curing of the precursor polyamic acid. It has already been reported[10-14] that PI formed from fluorine containing diamine (F-diamine) causes high pretilt angles.

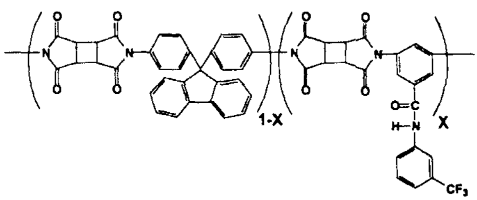

FIGURE 1 Chemical structure of PIs used.

LC cells were prepared to measure the dichroic ratios and pretilt angles of the LCs aligned by polarized UV exposed PI films. PI films were deposited on ITO glass substrates and then cured at 250 °C for 1 hr. The thickness of the PI film was controlled at 50 nm. The PI films were exposed with polarized UV at a number of incident angles to the PI surface[9]. We used a 450 W-Xe lamp (Oriel, model 6266) as a UV source, and a surface film polarizer (Oriel, model 27320) whose effective range is between 230 nm to 770 nm. The intensity of UV after passing through the polarizer was about 1 mW/cm^2 at 254 nm. LC cells were fabricated using two polarized UV exposed substrates with anti-parallel polarization axis. LC, ZLI-2293 (Merck), and dichroic LC, ZLI-2293 and 0.5 % M-618 (Mitsuitoatsu, λmax=550 nm), were filled into the cells in the isotropic state (120 °C) and slowly cooled to room temperature for measurement of pretilt angles and dichroic ratios of LC cells, respectively.

The dichroic ratios of the LC cells were measured using one polarizer and a UV-Vis spectrometer. We used crystal rotation method to measure pretilt angles below 15 ° and capacitive method to measure pretilt angels higher than 15 °.

RESULTS AND DISCUSSION

Figure 2 shows the relationship between the chemical structure of the PIs and the resulting pretilt angle of the LCs. The pretilt angles of LCs gradually increase with the molar fraction of F-diamine in PI. Furthermore, the direction of the pretilt angle coincides with that of the p-wave in the polarized UV light judging from the signs of symmetry points in the crystal rotation charts. In our previous papers[8,9], we

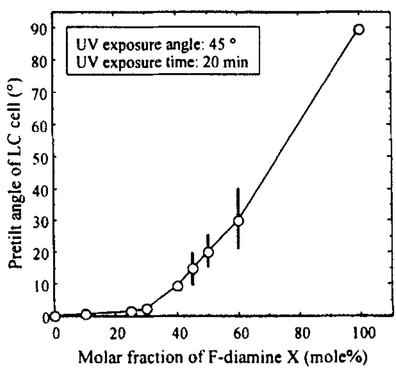

FIGURE 2 Dependence of pretilt angles on molar fraction of F-diamine in PI.

reported that the selective photo-decomposition of PIs parallel to the exposed polarization of UV light causes the randomization of PI main chains. The residual PI main chains perpendicular to the exposed UV polarization, which show no photo-decomposition, cause anisotropic van der Waals forces[15] which align the LC along the optic axis of PI. This means that the director of the LC is controlled by the polarization axis of UV light. We assume that the p-wave in polarized UV light generates pretilt angles along its polarization axis. We chose the PI containing 30 molar % of F-diamine (PI-30F) to analyze the behaviors of pretilt angles in more detail.

Figure 3 (a) shows the relationship between polarized UV exposure time and the pretilt angles of the LC cells at different exposure angles. Pretilt angles initially increase with polarized UV exposure angle and show maximum values for UV exposure time. Furthermore, UV exposure time required to produce the maximum pretilt angle gradually increases with UV exposure angles. We measured the dichroic ratios of the LC cells by changing the polarized UV exposure angles and UV exposure time. Figure 3 (b) shows the relationship between polarized UV exposure time and the dichroic ratios of the LC cells with different UV exposure angles. The dichroic ratios of the LC cells gradually increase with UV exposure time and reach a constant value of about 10.5, which is the same as that obtained using rubbed PI-30F alignment films. Furthermore, the dichroic ratios of the LC

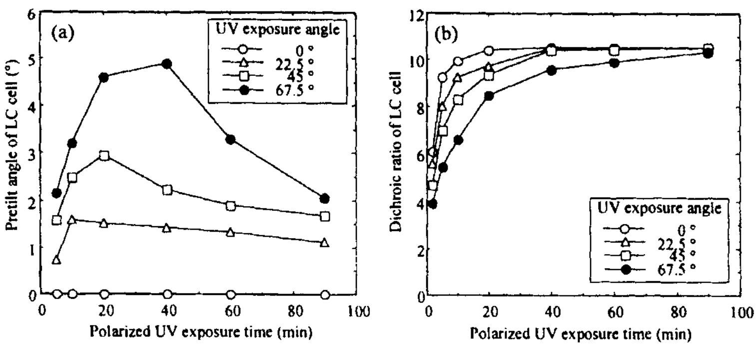

FIGURE 3 Relationship between polarized UV exposure time and pretilt angles (a) and dichroic ratios (b) of LC cells using PI-30F.

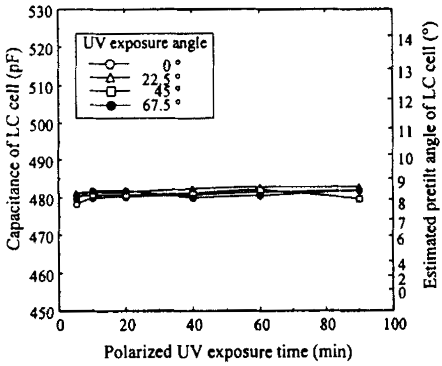

FIGURE 4 Relationship between polarized UV exposure time and capacitances of LC cells using PI-30F for various UV exposure angles.

cells increase with decrease of UV exposure angles at lower UV dosage. These results suggest that the alignment order of the LC on PI films with lower UV dosage or larger UV exposure angle is smaller than those with higher UV dosage or smaller UV exposure angle.

Figure 4 shows the capacitances of the LC cells as a function of UV exposure time. The estimated pretilt angle from the capacitance is also shown on right vertical axis. The capacitances of the LC cells show no change even thought changing UV exposure time and UV exposure angles, and the estimated pretilt angles are about 8 °. These results suggest that the surface pretilt angle on the PI film does not change before and after polarized UV exposure. Furthermore, the decrease of the pretilt angles observed in the LC cells with higher UV dosage, Fig. 3 (a), probably result not from the decomposition of F-diamine which generates high pretilt angle, but from breaking the surface order degeneracy of the LC molecules on PI films induced by polarized UV exposure as the same phenomenon observed in LC cell with rubbed PI film using a second harmonic generation technique[16,17].

To analyze the reason why pretilt angle shows the maximum value for UV exposure time, we measured the reflected UV light intensity (Fig. 5 (a)) from PI-ITO surface and the absorption spectrum of the PI-30F film (Fig. 5 (b)). The result of the reflected UV measurement at the incident UV angle of 67.5° to the surface

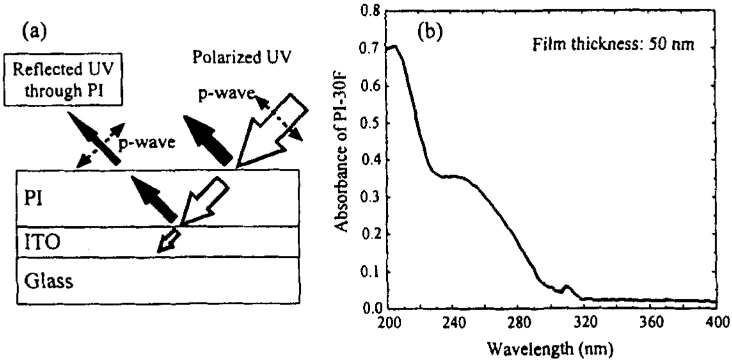

FIGURE 5 Reflected UV thought PI film (a) and absorption spectrum of PI-30F (b).

normal suggests that about 5 % of reflected UV light to the incident UV light can pass through PI film because of the low UV absorbance of PI-30F (Fig. 5 (b)). Furthermore, it should be noted that the direction of the p-wave in the reflected UV light is opposite to that in the incident UV light as shown in Fig. 5 (a).

To elucidate the mechanism of generation of pretilt angles in more detail, we measured the pretilt angles of the LC cells using PI films with double polarized UV exposure. First the PI film was exposed to polarized UV at an incident angle of 67.5

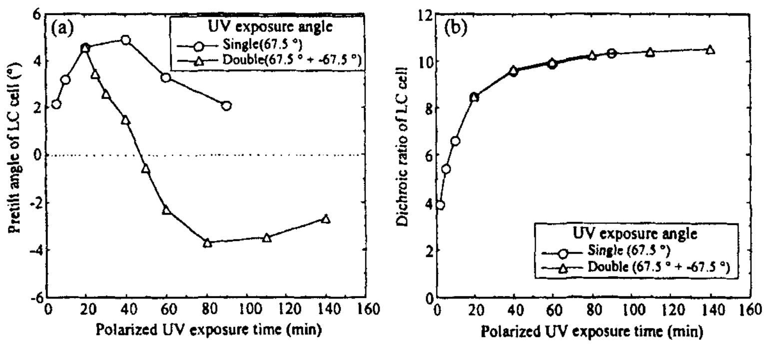

FIGURE 6 Relationship between polarized UV exposure time and (a) pretilt angles and (b) dichroic ratios of LC cells with single and double UV exposure.

° to the surface normal. Then film was exposed to polarized UV at the opposite incident angle of -67.5 °. Figure 6 (a) shows the relationship between polarized UV exposure time and the pretilt angles of the LC cells compared with single and double UV exposure. In this figure, a negative sign of pretilt angle after second UV exposure means that the direction of the pretilt angle caused by second UV exposure is opposite to that obtained by first UV exposure. In the case of single UV exposure, pretilt angles initially increase and show a maximum value for polarized UV exposure time. On the other hand, those after second UV exposure show steep decrease of pretilt angles, then show a negative maximum value, and gradually decrease for polarized UV exposure time.

Figure 6 (b) shows the relationship between polarized UV exposure time and dichroic ratios of LC cells compared with single and double UV exposure. The dichroic ratios of the LC cells monotonically increase with polarized UV exposure time, and there is no difference in the dichroic ratios of the LC cells using single or double UV exposure. These results suggest that the tilt angle direction of the LC can be easily controlled by the p-wave direction in the UV light.

Using these results, we can develop a hypothesis of the mechanism of generation of pretilt angles. Figures 7 show the in-plane configurations of the LC molecules on UV exposed PI during UV exposure. In Fig. 7 (a), arrows show the tilt angle directions of the LC molecules on PI film. Numbers which are

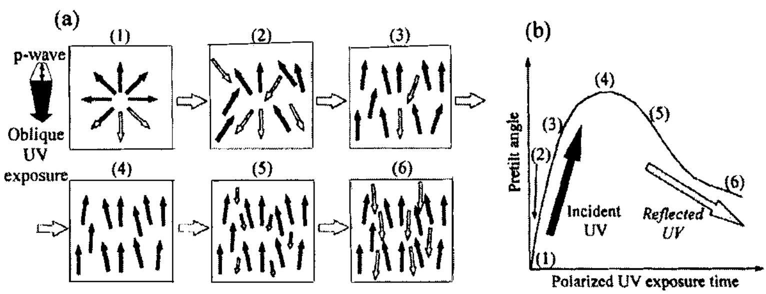

FIGURE 7 In-plane configurations of LC molecules on PI films (a) during polarized UV exposure (b): arrows show the tilt angle direction of LC.

corresponding to the in-plane configurations of the LC molecules shown in Fig. 7 (a) are also written in Fig. 7 (b). Before UV exposure the in-plane configuration of the LC molecules on PI film is random (Number 1). LC molecules tend to align with tilt angle direction along the direction of the p-wave in the UV polarization due to the decomposition of PI chains[8] (Number 2, 3). The resulting measured pretilt angles gradually increase with the degree of PI decomposition until its saturation (Number 4). Further UV exposure, however, gradually causes the decrease of the pretilt angle due to the reflected UV light from PI-ITO surface, whose p-wave direction is opposite to that in the incident UV light (Number 5, 6).

CONCLUSION

In this paper, we reported the mechanism of generation of the pretilt angles on PI films with a single linearly polarized UV exposure. Any desired pretilt angles from 0 ° up to 90 ° were obtained using PI films with different fluorine concentration. Pretilt angles also depended on the UV exposure time and UV exposure angles to the PI surface. We proposed that the pretilt angles on UV exposed PI films depend on the selective photo-decomposition of PI along the UV polarization which produces anisotropic van der Waals forces to align the LC along the optic axis of the PI. The dependence of pretilt angles of the LC on UV exposure conditions can be explained by breaking the degeneracy of the in-plane configurations of LC molecules during polarized UV exposure.

Acknowledgments

We acknowledge Drs. L. C. Chien, B. Taheri, and X. D. Wang of Kent State University and Dr. Yu. Reznikov of Institute of Physics of the Ukrainian National Academy of Science for their useful discussion. We also thank Drs. N. Bessho and Y. Matsuki of JSR Co. for their support in this research. Research was supported in part by NSF Science and Technology Center ALCOM, DMR 89-20147.

References

[1] A. Dyadyusha, V. Kozenkov, T. Marusii, Y. Reznikov, V. Reshetnyak, and A. Khizhnyak, *Ukrainian Fiz. Zh.*, **36**, 1059 (1991).

[2] M. Schadt, K. Schmitt, V. Kozinkov, and V. Chigrinov, *Jpn. J. Appl. Phys.*, **31**, 2155 (1992).

[3] M. Hasegawa and Y. Taira, *J. Photopolym. Sci. Tech.*, **8,** 703 (1995).
[4] J.L. West, X.D. Wang, Y. Ji, and J.R. Kelly, *Proc. SID,* **26,** 703 (1995).
[5] Y. Iimura, T. Saitoh, S. Kobayashi, and T. Hashimoto, *J. Photopolym. Sci. Tech.*, **8,** 258 (1995).
[6] K.Y. Han, B.H. Chae, S. H. Yu, J.K. Song, J.G. Park, and D.Y. Kim, *Proc. SID,* **27,** 707 (1997).
[7] M. Schadt, H. Seiberle, and A. Schuster, *Nature,* **381,** 212 (1996).
[8] M. Nishikawa, B. Taheri, and J.L. West, *Appl. Phys. Lett.*, **72,** 2403 (1998).
[9] M. Nishikawa, B. Taheri, and J.L. West, *Proc. SID,* **29,** 131 (1998).
[10] M. Nishikawa, T. Miyamoto, S. Kawamura, Y. Tsuda, N. Bessho, D. -S. Seo, Y. Iimura, and S. Kobayashi, *Mol. Cryst. Liq. Cryst.*, **258,** 285 (1995).
[11] M. Nishikawa, Y. Matsuki, N. Bessho, Y. Iimura, and S. Kobayashi, *J. Photopolym. Sci. Tech.*, **8,** 233 (1995).
[12] M. Nishikawa and Y. Takeuchi, *Display and Imaging,* **3,** 353 (1995).
[13] Y. Momoi, J. Stohr, and M.G. Samant, *Proc. IDRC,* **17,** 73 (1997).
[14] K. Shirota, K. Ishikawa, H. Takezoe, A. Fukuda, and T. Shiibashi, *Jpn. J. Appl. Phys.*, **34,** L316 (1995).
[15] K. Okano, M. Matsuura, and S. Kobayashi, *Jpn. J. Appl. Phys.*, **21,** L109 (1982).
[16] M.B. Feller, W. Chen, and Y.R. Shen, *Phys. Rev.*, **A43,** 6778 (1991).
[17] M. Barmentlo, R.W.J. Hollering, and N.A.J.M. van Aerle, *Phys. Rev.* **A46,** R4490 (1992).