Thermal Stability of LC Alignment Layers Prepared by UV Exposure During Imidization of Polyimide

Jae-Hoon Kim, Young-Jun Seo, Bharat R. Acharya[1], D□na Mae Agra[1] and Satyendra Kumar[1]

Department of Physics, Hallym University, Chunchon, Kangwon-Do 200-702, Korea

[1]Department of Physics, Kent State University, Kent, Ohio 44242, US

A novel method for liquid crystal alignment using in-situ exposure to linearly polarized ultra-violet (LPUV) light during imidization of polyimide has been devised. The alignment layers prepared by this method exhibit higher thermal stability than the conventional method that employs LPUV exposure after imidization. Multi-domain cells can be easily fabricated with the use of a photo mask and multi-step in-situ LPUV exposure during hard bake. With this method, it is also possible to generate pretilt angle using two-step LPUV exposure during imidization.

I. Introduction

Technologically, how to achieve liquid crystal alignment on substrates is crucial to have a reliable procedure that permits good control of alignment and yields high-quality alignment of liquid crystal (LC) used in electro-optic devices[1]. Photo-alignment using polyimide (PI) has emerged as a promising non-contact technique because of its simplicity and easy control of the alignment direction and anchoring energy, so that multi-domain devices, with improved viewing angle characteristics[2-8]. However, under this method the LPUV exposure is carried out after the imidization of the film is complete. The PI alignment layers prepared by this method possess poor thermal and chemical stability. Evidently, many researches are attempting to develop new non-contact alignment method for producing stable alignment layer. In order to improve the thermal stability of prepared alignment layer, we proposed new non-contact UV alignment method which employs LPUV exposure during the imidization of PI [9].

In this paper, we report detail experimental results about the thermal stability of the alignment layers prepared by the new method.

II. Experimental

We tested the in-situ method using several PIs from various chemical companies. The main PIs used in this study are the PI SE610, 7311, and 7511 (Nissan Chemical Co.). And the nematic LC E48 (British Drug House) is used to make LC cells. Glass substrates were spin coated with a solution of PAA (unimidized PI) in N-methyl-2-pyrrolidinone at 3000 rpm for 30 s. The films were then soft baked at 100 °C for 10 min to evaporate the solvent. The imidization temperatures of PAA films are depending on the PIs used. During the hard bake, the precursor PAA film undergoes imidization forming PI. In the conventional method, the spin coated PI film followed by thermal imidization is exposed to LPUV at room temperature [2,3,5-8]. In our study, we exposed LPUV for 30 min during thermal imidization (or hard bake). To distinguish it from the conventional method, we are calling it an in-situ UV exposure method.

Fig. 1 shows schematically the experimental setup.

A collimated beam from a Xe lamp was polarized using an Oriel UV sheet polarizer. The intensity of the polarized UV light was approximately 6 mW/cm^2 at the film's surface. The PI/PAA coated substrate was placed perpendicular to the polarized UV beam with the polymer side toward the lamp. The hot stage can be rotating for oblique LPUV exposure for pre-tilt angle generation.

We measured the optical anisotropy induced by LPUV during exposure as shown in Fig. 1. We used a photo-elastic modulator (PEM90, Hinds Instruments) with a fused silica head and a He-Ne laser for optical phase retardation measurements. The photo-elastic modulator (PEM) was placed between two crossed polarizers with its optic axis at 45° to the axes of polarizer and analyzer. The LC cell prepared with photo-alignment layers was placed between PEM and the analyzer. The signal from the photo detector was fed to a lock-in amplifier (EG&G Princeton Applied Research, Model 5210) for measuring the ac signal and a digital multimeter for the dc signal. The lock-in amplifier was tuned to the 50 kHz reference signal from PEM. The laser beam was incident normal to the sample cell's surface. The signal was monitored

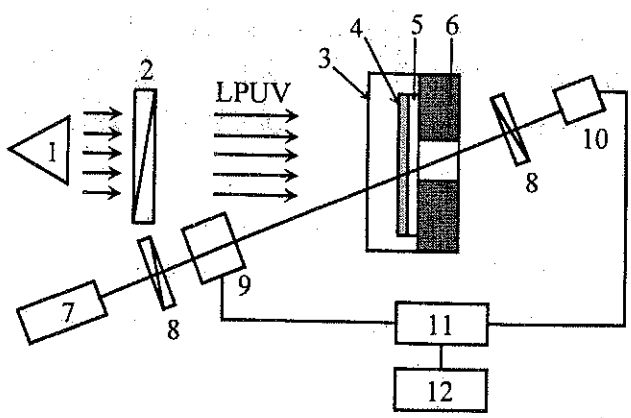

Fig. 1. The schematic diagram of experimental setup; (1) UV source, (2) UV polarizer, (3) UV transparent window, (4) PAA layer, (5) Glass substrate, and (6) Hot stage, (7) He-Ne laser, (8) Polarizers, (9) PEM, (10) Detector, (11) Lock-in amplifier, (12) Computer.

while rotating the sample with respect to the surface normal. The sensitivity of this method enables us to measure the phase retardation with a precision of ± 0.01°.

III. Results and Discussion

The optical anisotropy was shown in Fig. 2 as a function of the angle of rotation for various PI films (AL1051, SE1132, and JALS214R) prepared by in-situ method. Though the magnitude is different for different PI films, it is very clear that the optical anisotropy is induced by LPUV exposure during imidization. We note that the magnitude of the optical anisotropy is depending on the hard baking temperature, UV intensity, exposure time, thickness of films, and so on.

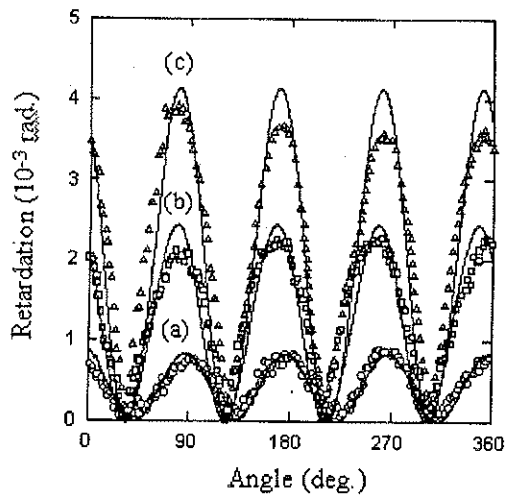

Fig. 2. Optical phase retardation as a function of the rotation angle of the sample for (a) AL 1051 (b) SE 1132, and (c) JALS 214R PI films. The LPUV is exposed 30 min during imidization.

The dependence of optical retardation to the UV exposure time for the in-situ method is shown along with that of conventional film for comparison in Fig. 3. We believe that there are several factors responsible for the enhancement in optical retardation for the in-situ method. In conventional method, the LPUV dissociates bonds in polymer chains after polymerization

(imidization) had completed. As a result, smaller chains (segments) are left in the direction of polarization while the orthogonal direction is populated by longer chains[6]. The smaller segments are not able to relax and perhaps reorient as the UV exposure is conducted at room temperature. Consequently, there is significant strain energy stored in these films which is released at higher temperatures during thermal annealing. This relaxation process renders the polymer chain orientation more random which in turn loses the ability to align liquid crystal molecules. On the other hand, in the in-situ method, the depolymerization by LPUV and polymerization by thermal reaction occur simultaneously. Therefore, the imidization rate is anisotropic. Moreover, since we expose LPUV at high temperature in the in-situ method, the mobility of polymer chains is higher. Small polymer chains that reorient and become perpendicular to the direction of polarization are likely to undergo imidization and thus increase the number and length of the chains in that direction. Thus, we can expect that the resulting alignment films are not only free of strain energy and hence more stable than the conventionally prepared films.

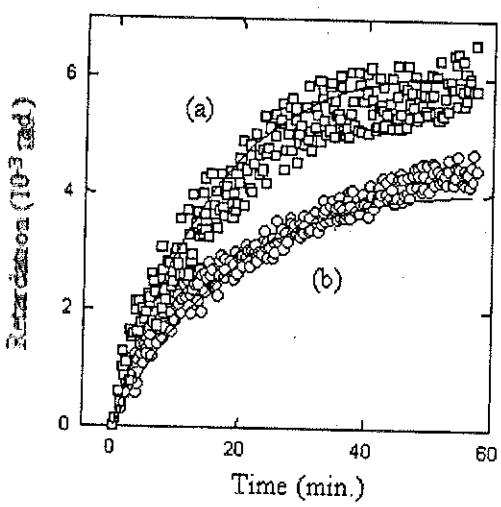

Fig. 3. Comparison of optical phase retardation of SE 610 PI as a function of the LPUV exposure time for (a) in-situ method and (b) conventional method. The imidization temperature was 250 °C.

The LC texture in a cell prepared with the alignment layer using the conventional method is initially uniform as shown in Fig. 4(a). However after thermal annealing at 100 °C for 12 h, it shows schlieren texture indicating that the LC molecules have lost their alignment [Fig. 4(b)]. The optical texture of the cell prepared by the in-situ method is also uniform over the whole area as shown in Fig. 4(c). After thermal annealing under similar conditions, no degradation of alignment is observed [Fig. 4(d)]. From the result, it is clear that the in-situ method produces more thermally stable alignment layers than conventional method. It is believed that this method holds the promise of producing even more stable alignment layers, when all parameters, such as temperatures of soft- and hard-bake, intensity of UV, duration, and the time of UV exposure, have been optimized.

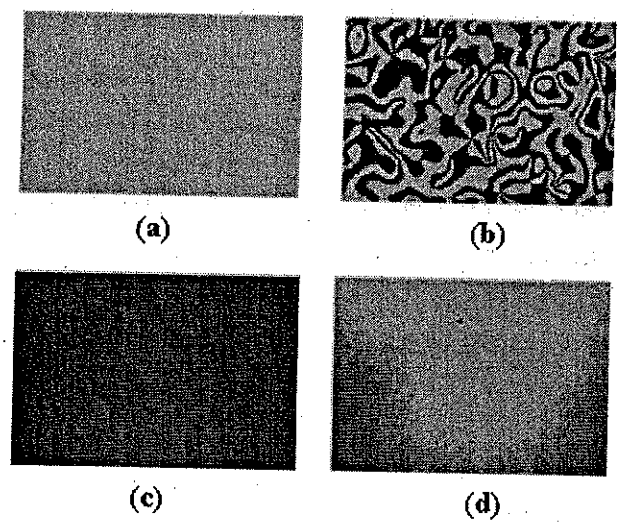

Fig. 4. Polarizing microscopy textures of a homogeneously aligned cell prepared by conventional [(a) and (b)] and in-situ [(c) and (d)] methods: (a), (c) before and (b), (d) after thermal annealing at 100 °C for 12 h.

In Table I, we compare the thermal stability at 100 °C for various alignment methods using SE 7311 and 7511. The UV intensity and exposure time are 400W and 60 min, respectively. Among the

method, the rubbing produces the most stable alignment layers as expected. However, for both PIs, the thermal stability of in-situ sample is better than that of conventional method. And SE7311 shows better thermal stability than SE7511. It is probably due to the different chemical structure of both PIs.

Table I : Thermal stability for different alignment methods for SE 7311 and 7511.

PI	Method	Annealing time (h) 0	24	48	72	96
SE 7311	Rubbing	↑	↑	↑	↑	↑
	Conventional	↑	↑	↑	🔒	🔒
	In-Situ	↑	↑	↑	↑	🔒
SE 7511	Rubbing	↑	↑	↑	↑	🔒
	Conventional	↑	↑	🔒	🔒	🔒
	In-Situ	↑	↑	↑	🔒	🔒

↑ : Alignment texture is uniform
🔒 : Disclination line or micro-domain appears

Now, we studied the influence of UV exposure time on thermal stability in in-situ method for SE 7311. The UV intensity was 400W, and annealing temperature was 100 °C. The results are summarized in Table II. The samples with LPUV exposure for 30 min and 40 min show the most stable alignment capabilities. Longer UV exposure than 40 min decrease the thermal stability. This may be due to the fact that the prolonged UV exposure eventually dissociates even the bonds oriented perpendiculay to the polarization direction.

Table II : Thermal stability for varying UV exposure time for SE 7311.

Exposure time (min)	Annealing time (h) 0	24	48	72	96	108	132
60	↑	↑	↑	↑	🔒	🔒	🔒
50	↑	↑	↑	↑	🔒	🔒	🔒
40	↑	↑	↑	↑	↑	↑	🔒
30	↑	↑	↑	↑	↑	↑	🔒

↑ : Alignment texture is uniform
🔒 : Disclination line or micro-domain appears

IV. Concluding Remarks

In conclusion, we have demonstrated a novel method for LC alignment using LPUV exposure during imidization of polyimide. The results show that samples prepared by this method have better thermal stability and require less processing time. We note that this method may also be applicable to other photopolymer films during evaporation of the solvent and to solutions of a cross-linkable resin and a curing agent.

Acknowledgements

This work was supported in part by NSF Science and Technology Center ALCOM grant DMR-89-20147, and by the Korea Science and Engineering Foundation Grant #2001-2-11400-003-02.

REFERENCES

1) J. Cognard: *Alignment of Nematic Liquid Crystals and Their Mixtures*, Mol. Cryst. Liq. Cryst. Suppl. 1 (1982) Chap. 1, p. 6.
2) M. Hasegawa and Y. Taira: J. Photopolym. Sci. Technol. **8** (1995) 241.
3) J. L. West, X. Wang, Y. Li and J. R. Kelly, SID Dig. **XXVI** (1995) 703.
4) J. Chen, D. L. Johnson, P. J. Bos, X. Wang and J. L. West: Phys. Rev. E, **54** (1996) 1599.
5) J. -H. Kim, Y. Shi, S. -D. Lee and S. Kumar: Appl. Phys. Lett. **71** (1997) 3162.
6) J. -H. Kim, S. -D. Lee and S. Kumar: Phys. Rev. E **57** (1998) 5644.
7) M. Nishikawa, B. Taheri and J. L. West: Appl. Phys. Lett. **72** (1998) 2403.
8) C. E. Hoyle and E. T. Anzures: J. Appl. Polym. Sci. **43** (1991) 1.
9) J. -H. Kim, B. R. Acharya, S. Kumar and K. R. Ha: Appl. Phys. Lett. **73** (1998) 3372.