

## Thermal Stability of Liquid Crystal Alignment Layers Prepared by *In-Situ* Ultra-Violet Exposure during Imidization of Polyimide

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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.

KEYWORDS: liquid crystals, alignment layer, UV exposure

### 1. 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. Surface treatments, such as, obliquely evaporated SiO<sub>x</sub> layers, Langmuir-Blodgett films, rubbed polymer films have been used to obtain homogeneous alignment of LCs.<sup>1)</sup> Among them, mechanical rubbing of polyimide (PI) layers is the most common alignment method used in mass production of LC displays because of its simplicity and high thermal stability of the resultant alignment. The disadvantages of the rubbing method are the generation of dust particles, electro-static charge, and physical damage which are detrimental to the fabrication of thin film transistor based devices.

In recent years, photo-alignment 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. It has been demonstrated that poly(vinyl)4-methoxycinnamate and poly(vinyl)cinnamate films, when anisotropically cross-linked using linearly polarized ultra-violet (LPUV) light, can be very effective as alignment layer.<sup>2,3)</sup> However, their performance deteriorates with time.

More recently, several research groups have reported alignment of LC's by PI films exposed to the LPUV light.<sup>4-9)</sup> Fourier transform infrared (FTIR) spectroscopy has shown that the UV irradiation anisotropically photo-dissociates photosensitive chemical bonds in PI including those in the imide ring.<sup>10)</sup> This reduces the polarizability of PI molecules<sup>6)</sup> and changes the surface morphology.<sup>8)</sup> 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.<sup>11)</sup>

In this paper, we report detail experimental results about the thermal stability of the alignment layers prepared by the new method. The alignment layers prepared by this method has much higher thermal stability than of the alignment layers prepared by the conventional UV method for PI films. And also, we report the pretilt angle generation using two-step *in-situ* LPUV exposure during hard bake.

### 2. 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. PI films were prepared by heat curing of precursor polyamic acid (PAA) solutions which was synthesized from the reaction between tetracarboxylic dianhydride and diamines. 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. We followed the recommendation temperature from the companies. In case of SE610, it is hard baked at 250°C for 1 h. 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.<sup>4,5,7-9)</sup> 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.

Figure 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<sup>2</sup> 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 pretilt 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 mea-

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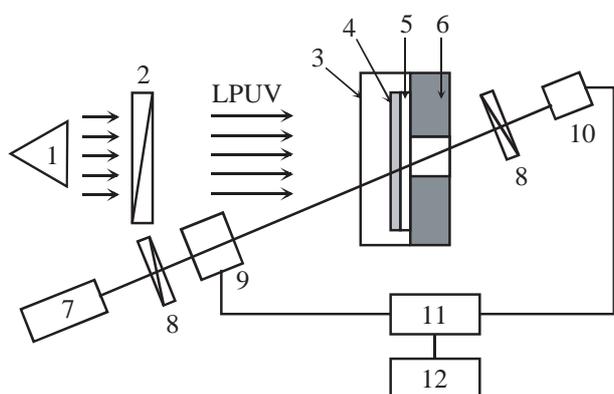


Fig. 1. The schematic diagram of experimental setup; (1) UV source, (2) UV polarizer, (3) UV transparent window, (4) PAA layer, (5) Glass substrate, and (6) Hot stage, (7) He-Ne laser, (8) Polarizers, (9) PEM, (10) Detector, (11) Lock-in amplifier, (12) Computer. The sample hot stage is mounted such that it can be rotate for oblique exposure to generate finite pretilt.

measurements. The photo-elastic modulator (PEM) was placed between two crossed polarizers with its optic axis at  $45^\circ$  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 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  $\pm 0.01^\circ$ .

### 3. Results and Discussion

The optical anisotropy was as a function of the angle of rotation for various PI films (AL1051, SE1132, and JALS214R) prepared by *in-situ* method (see Fig. 2). 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. With comparing rubbed sample, the magnitude of the retardation is comparable but has the opposite sign to that of the rubbed film. This suggests that the polymer chains are aligned perpendicularly to the direction of polarization of LPUV. From FTIR study, we find that, the orientation of PI molecules change after LPUV exposure and appears to be primarily due to preferential degradation of PI molecules parallel to the electric field of LPUV.<sup>11)</sup> Reorientation of PI chains due to breaking of imide bonds may be contributing to the optical anisotropy and alignment of LC molecules. The broken bonds reduce the polarizability of the PI molecules. In contrast to the previous report that the LC alignment is mainly achieved via the interactions of LC molecules with the polar functional group in PI produced by LPUV,<sup>4)</sup> our results show that anisotropic irreversible depolymerization is primarily responsible for LC alignment on LPUV exposed PI films during the imidization.

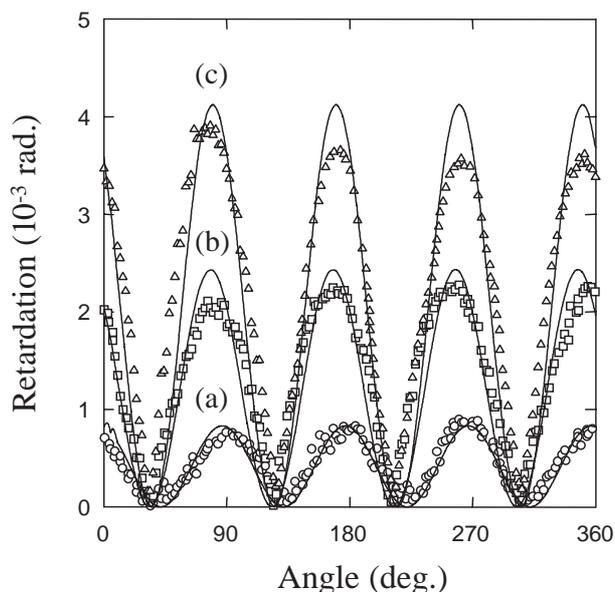


Fig. 2. Optical phase retardation as a function of the rotation angle of the sample for (a) AL 1051 (b) SE 1132, and (c) JALS 214R PI films. The LPUV is exposed 30 min during imidization.

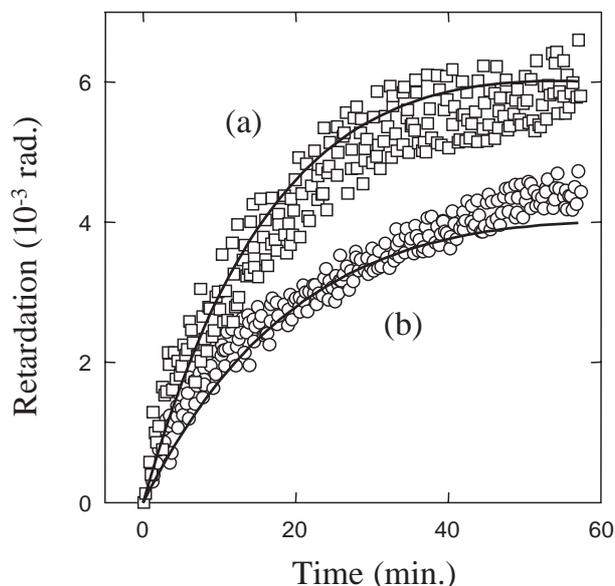


Fig. 3. Comparison of optical phase retardation of SE 610 PI as a function of the LPUV exposure time for (a) *in-situ* method and (b) conventional method. The imidization temperature was  $250^\circ\text{C}$ .

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. In order to remove thickness effect, we measured the optical retardation in the same sample: we covered one half of the sample by a photo-mask during imidization and we measured optical retardation in the second half exposed to LPUV during imidization. After then, we cooled down the temperature and exposed LPUV in the first half of the sample with measuring optical retardation. The optical anisotropy gradually increases with the exposure time and becomes saturated in 1 h in both methods. And it is clear that the magnitude of retardation for the sample prepared by *in-situ* method is larger than of the sample prepared by conventional method.

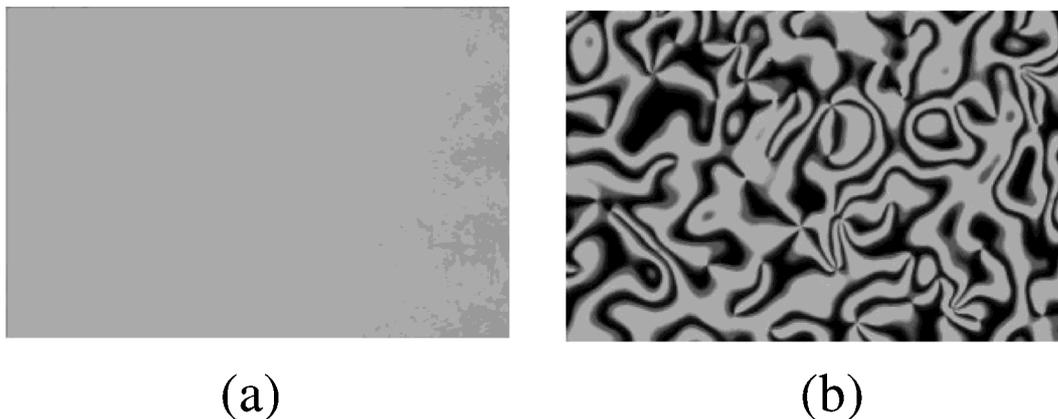


Fig. 4. Polarizing microscopy texture of a homogeneously aligned cell prepared by conventional UV method, (a) before and (b) after thermal annealing at 100°C for 12 h. The loss alignment in (b) shows thermal instability of this alignment method.

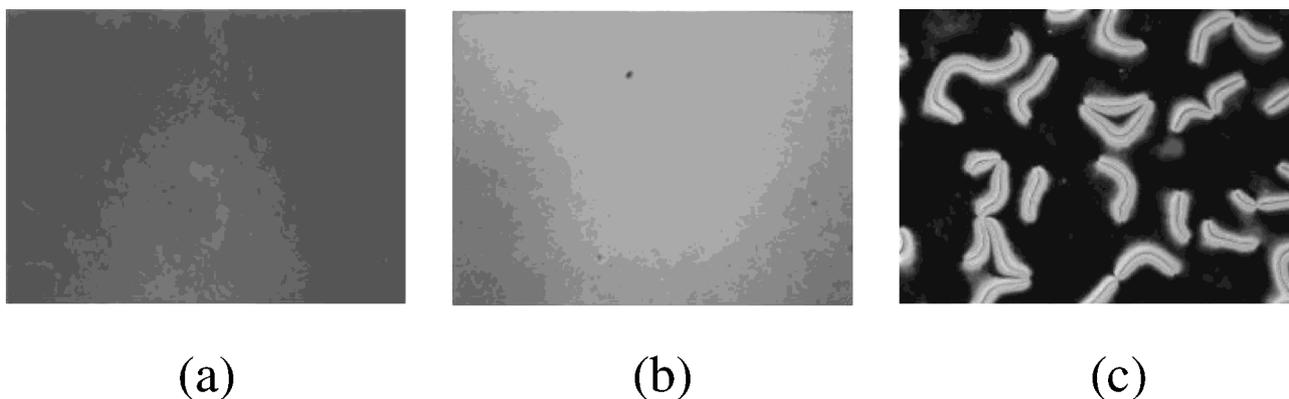


Fig. 5. Polarizing microscopy texture for a homogeneously aligned nematic cell prepared by the *in-situ* UV exposure method, (a) before and (b) after thermal annealing at 100°C for 12 h, and (c) after thermal annealing at 150°C for 12 h. Evidently, the alignment is more stable compared to that of the conventional method shown in Fig. 4.

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.<sup>8)</sup> 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.

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. 5(a). After thermal annealing under similar conditions, no degradation of alignment is observed [Fig. 5(b)]. At elevated temperature (150°C for 12 h), some loss of alignment is observed as shown in Fig. 5(c). 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.

To optimize the bake temperature, for SE7311 and 7511, we measured optical anisotropy as a function of baking temperature as shown in Fig. 6. Both PIs show higher retardation at 200°C than other temperatures. So, we fixed imidization temperature at 200°C for further investigation.

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 400 W 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

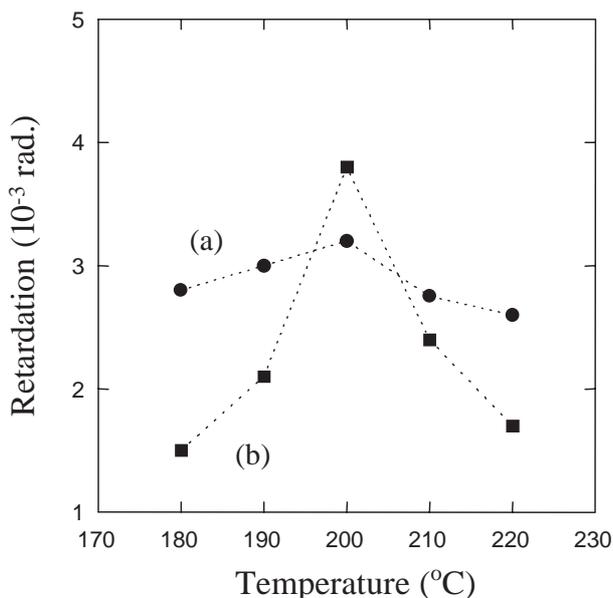


Fig. 6. Optical phase retardation as a function of imidization temperature for (a) SE 7311 and (b) SE 7511. The UV intensity and exposure time were 400 W and 30 min.

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	○	○	○	×	×
	<i>In-Situ</i>	○	○	○	○	×
SE 7511	Rubbing	○	○	○	○	×
	Conventional	○	○	×	×	×
	<i>In-Situ</i>	○	○	○	×	×

○: Alignment texture is uniform.  
 ×: Disclination line or micro-domain appears.

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

UV 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.

conventional method. And SE7311 shows better thermal stability than SE7511. It is probably due to the different chemical structure of both PIs.

Now, we studied the influence of UV exposure time on thermal stability in *in-situ* method for SE 7311. The UV intensity was 400 W, 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

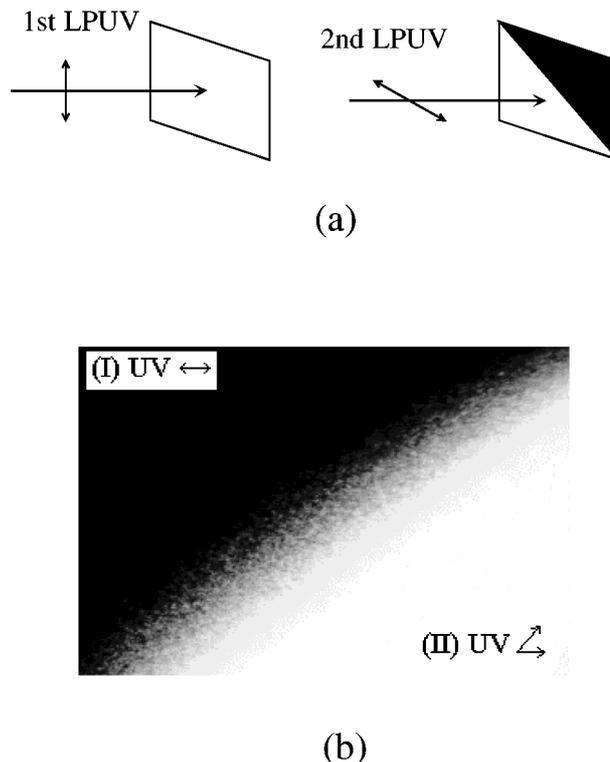


Fig. 7. (a) Schematic drawing of experimental set-up for multi-domain cells. (b) Appearance of a homogeneously aligned multi-domain cell between crossed polarizers. The polarization direction of first exposed LPUV coincides with the axis of one of the crossed polarizers. The polarization direction was at 45° to the polarizer axes as shown in the figure. Dark(bright) regions marked as I(II) represent one(two) LPUV exposure(s).

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 perpendicularly to the polarization direction.

Since, in the *in-situ* method, LPUV exposure takes place during imidization of PI, the processing time are significantly reduced compared to the conventional process. Moreover, multi-domain cells can be easily fabricated with multi-step LPUV exposure using a photo mask during the hard bake [Fig. 7(a)]. In our study, whole area of the substrate was exposed to normally incident LPUV for the first 20 min of hard baking. During the next 20 min of hard baking, one half of the substrate was covered by a photo-mask and the second half was exposed normally to LPUV with polarization direction rotated by 45° with respect to the first exposure. Figure 7(b) shows the microscopic texture of the sample. In one region (marked as I), which is exposed to LPUV only once, the polarization direction of the LPUV exposure coincides with the axis of one of the cross polarizers and minimum transmittance is obtained, as expected. The other region (marked as II), with two LPUV exposures with polarization direction rotated through 45° during the second exposure, appears bright.

In applicational aspects, the generation of pretilt angle is one of the most important factors to eliminate orientational defects which significantly deteriorate the performance of LC displays. We tested the pretilt angle generation using *in-situ* method by the same method using in conventional method, i.e. two-step UV exposure method. Whole area of the substrate was exposed to normally incident LPUV for the first

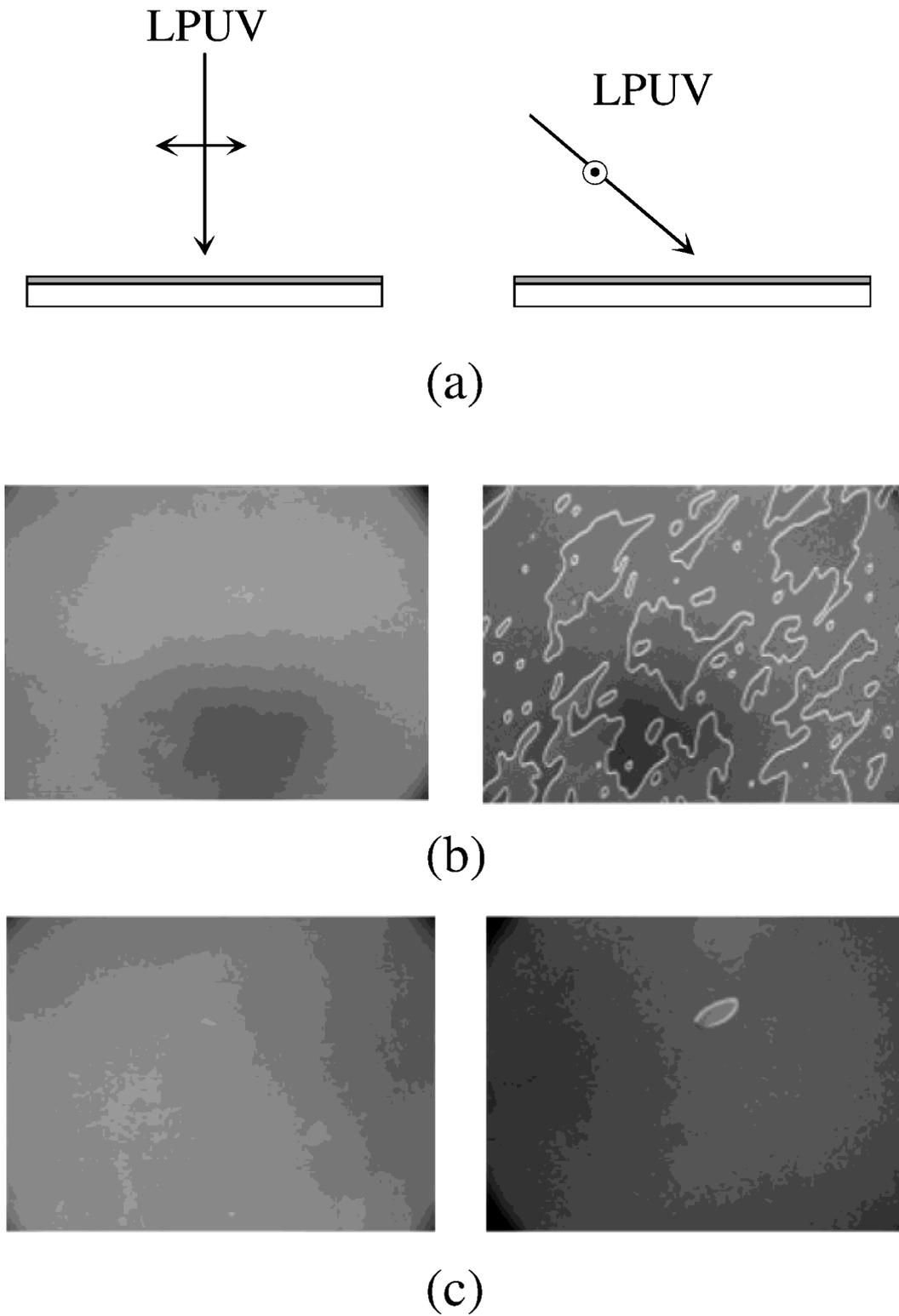


Fig. 8. (a) Schematic drawing of experimental set-up for generating pretilt angle. (b) Alignment textures between crossed polarizers for single LPUV exposure with different applied voltages. (c) Alignment textures between crossed polarizers for double LPUV exposure with different applied voltages. Applied voltage was 1 V (left) and 3 V (right) in (b) and (c).

20 min of hard baking. During the next 10 min of hard baking, LPUV with polarization direction rotated by  $90^\circ$  with respect to the first exposure is exposed obliquely [Fig. 8(a)]. Figures 8(b) and 8(c) are textures of the samples for single LPUV exposure with normal direction to the substrates and double LPUV exposure as described above, respectively, with different applied voltages. In low voltage regime, both sam-

ples show uniform alignment. In higher voltage, however, it appears disclination lines in single exposed sample due to reverse tilt. It means that the pretilt angle for this sample is nearly zero. In double exposed sample, it still shows uniform alignment which means finite pretilt angle is generated on the surface. Using the crystal rotation method, we found that the pretilt angle is about  $3^\circ$ .

#### 4. 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. And also, we can easily make multi-domain alignment layers and generate pretilt angles using multi-step UV exposure. 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.

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