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A method for liquid crystal alignment using *in situ* ultraviolet exposure during imidization of polyimide

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Homogeneous alignment of liquid crystals can be achieved by a technique using polyimide films and *in situ* exposure to linearly polarized ultraviolet (LPUV) light during imidization. The alignment layers prepared by this method exhibit higher thermal stability while requiring shorter processing time than the conventional UV alignment method which employs UV exposure after the imidization of polyimide is complete. Multidomain cells can be easily fabricated with the use of a photomask and multistep *in situ* LPUV exposure during hard bake. © *1998 American Institute of Physics.* [S0003-6951(98)02949-0]

The preparation of highly oriented liquid crystals (LCs) is of great importance for the basic understanding of interfacial phenomena and for the operation of electro-optical devices. Substrates with obliquely evaporated SiO layers, Langmuir–Blodgett films, rubbed polymer films, and linearly photopolymerized films possess anisotropic surface potential and have been successfully used to align liquid crystals.[1–4]

Mechanical rubbing of polyimide (PI) layers is the most common alignment method used in mass production of liquid crystal displays (LCDs) because of its simplicity and high thermal stability of the resultant alignment. The disadvantages of the rubbing method are the generation of dust particles, electrostatic charge, and physical damage which are detrimental to the fabrication of thin film transistor based devices.

To eliminate these problems, nonrubbed (noncontact) photoalignment processes have been developed in recent years. It has been demonstrated that poly(vinyl)4-methoxycinnamate (PVMC) and poly(vinyl)cinnamate films, when anisotropically cross linked using linearly polarized ultraviolet (LPUV) light, can be very effective as alignment layers.[2,3] However, their performance deteriorates with time. Recently, the alignment of LCs by PI films exposed to the LPUV light has been reported.[5–9] The photoalignment method allows for an easy control of the alignment direction and anchoring strength so that multidomain devices, with improved viewing angle characteristics, can be readily produced. 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 researchers are attempting to develop new noncontact alignment methods for producing a stable alignment layer.

In this letter, we report the development of a noncontact UV alignment method for LCs. The alignment layers prepared by this method have much higher thermal stability than of the alignment layers prepared by the conventional UV method for PI films. This method can be applied to any UV sensitive polymer film to produce an alignment layer.

The materials used in this study are the PI SE610 (Nissan Chemical Co.) and the nematic LC E48 (British Drug House). 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 PAA film was then imidized by hard baking at 250 °C for 1 h. In the conventional method, the spin coated PI film followed by thermal imidization is exposed to LPUV at room temperature.[5,6] In our study, we exposed LPUV for 30 min during thermal imidization (or hard bake) at 250 °C. 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 UV light from a Xe lamp was polarized

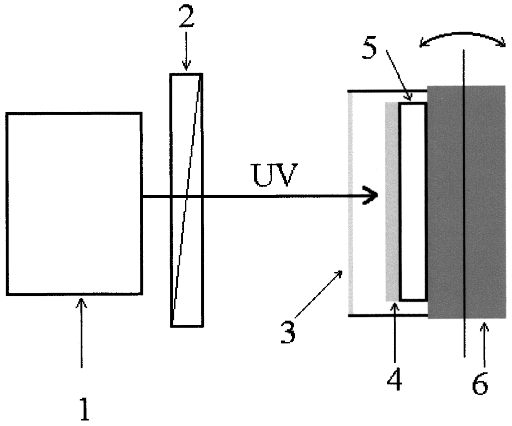

FIG. 1. Schematic diagram of experimental setup; (1) UV source, (2) UV polarizer, (3) UV transparent window, (4) PAA layer, (5) glass substrate, and (6) hot stage. The sample hot stage is mounted such that it can be rotated for oblique exposure to generate finite pretilt.

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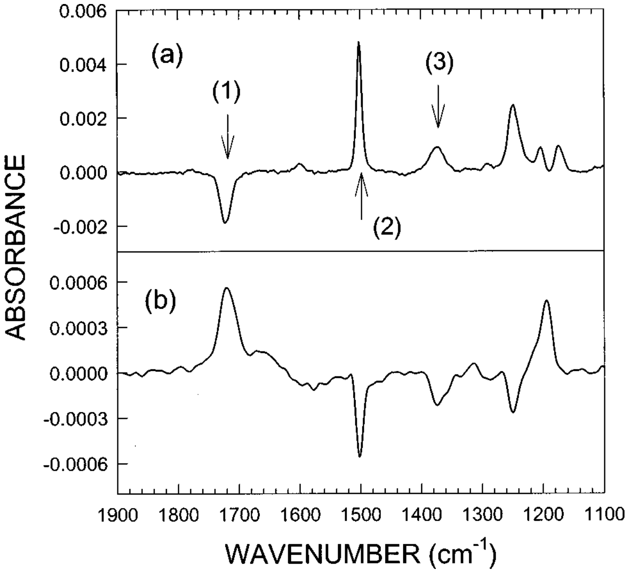

FIG. 2. The polarized FTIR spectra obtained by subtracting the spectra taken with IR polarization parallel to the rubbing direction or the direction of polarization of LPUV from the spectrum taken with IR polarization perpendicular to the respective direction for (a) rubbed PI film and (b) PI film prepared by the *in situ* method. Peaks (1), (2), and (3) are attributed to the ν(C=O), ν(1,4-C_6H_4), and ν(imide C–N–C), respectively.

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.

PI/PAA films spun onto CaF_2 were used for the measurement of Fourier transform infrared (FTIR) spectra using Magna 550 FTIR (Nicolet) spectrometer. From the collected FTIR spectrum, the CaF_2 spectrum was subtracted to obtain the contribution of the sample. A single diamond IR polarizer from Harrick Co. was used for this study. To reduce the noise level, over 300 scans were obtained at a resolution of 4 cm^{-1}.

Figure 2 shows the difference of the polarized IR spectrum obtained by subtracting the spectrum taken with polarization parallel and perpendicular to the rubbing direction and the polarization vector of LPUV. The peaks at 1722, 1503, and 1377 cm^{-1} are attributed to the ν(C=O), ν(1,4-C_6H_4), and ν(imide C–N–C), respectively. Although the transition moment of C=O bonds is perpendicular to the main chain direction, those of C_6H_4 and CNC functional groups are parallel to the main chain direction. In the rubbed sample, the absorbance is positive at 1503 and 1377 cm^{-1}, and negative at 1722 cm^{-1}. It indicates that rubbed PI chains are oriented along the rubbing direction. In contrast to the rubbed sample, the difference absorption spectra of the sample prepared by *in situ* method is quite the opposite; negative values at 1503 and 1377 cm^{-1}, and positive value at 1722 cm^{-1}. The reverse sign of each of the components in the two samples suggests that the orientation of the unreacted PI molecules is perpendicular to the polarization direction of LPUV. The change in PI's molecular orientation after LPUV exposure appears to be primarily due to a preferential degradation of the PI molecules along the direction of polarization of LPUV. Reorientation of the molecular chain due to the imide bond breaking may also play a role.

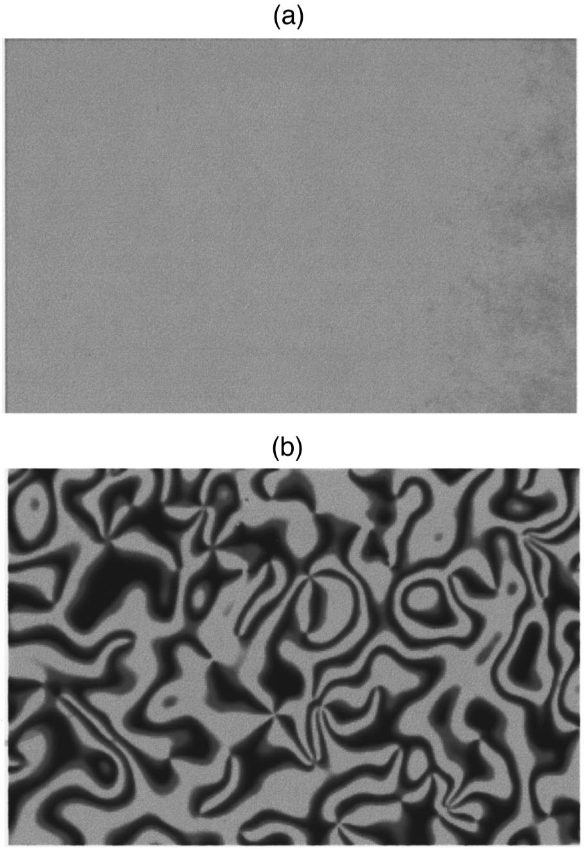

FIG. 3. Polarizing microscopy texture of a homogeneously aligned cell prepared by conventional UV method: (a) before and (b) after thermal annealing at 100 °C for 12 h. The loss of alignment in (b) shows thermal instability of this alignment method.

The LC texture in a cell prepared with the alignment layer using the conventional method is initially uniform as shown in Fig. 3(a). However after thermal annealing at 100 °C for 12 h, it shows schlieren texture indicating that the alignment is lost [Fig. 3(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(a). After thermal annealing under similar conditions, no degradation of alignment is observed [Fig. 4(b)]. At elevated temperature (150 °C for 12 h), some loss of alignment is observed as shown in Fig. 4(c). Clearly, the *in situ* method yields much more stable alignment layers than the conventional method. It is expected that this method can be further developed to provide even higher thermal stability.

We believe that there are several factors responsible for the enhancement in thermal stability for the *in situ* method. In the conventional method, the LPUV dissociates bonds in polymer chains after polymerization (imidization) had been completed. As a result, smaller chain (segments) are left in the direction of polarization while the orthogonal direction is populated by longer chains.[8] 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

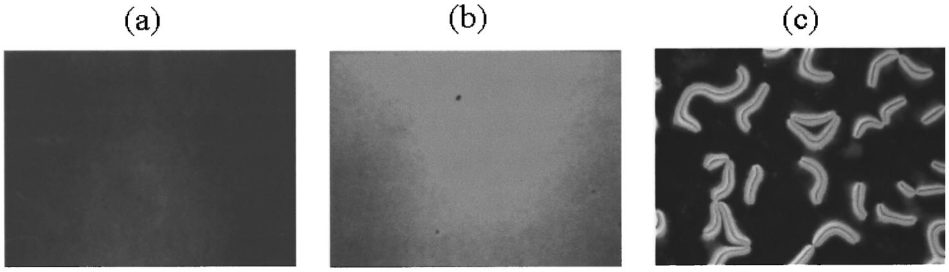

FIG. 4. Polarizing microscopy texture for a homogeneously aligned nematic cell prepared by the *in situ* UV exposure method: (a) before and (b) after thermal annealing at 100 °C for 12 h, and (c) after thermal annealing at 150 °C for 12 h. Evidently, the alignment is more stable compared to that of the conventional method shown in Fig. 3.

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, the resulting alignment films are not only free of strain energy and hence more stable, they are more effective than the conventionally prepared films. 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.

Since, in the *in situ* method, LPUV exposure takes place during imidization of PI, the number of steps in preparing an alignment layer and the processing time are significantly reduced compared to the conventional process. Moreover, multidomain cells can be easily fabricated with multistep LPUV exposure using a photomask during the hard bake. In our study, the 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 photomask and the second half was exposed normally to LPUV with polarization direction rotated by 45° with respect to the first exposure. Figure 5 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. The minimum transmission for this region is obtained by rotating the LC cell through 45° showing that the LC alignment direction has changed by 45° and is perpendicular to the polarization direction of the second LPUV exposure.

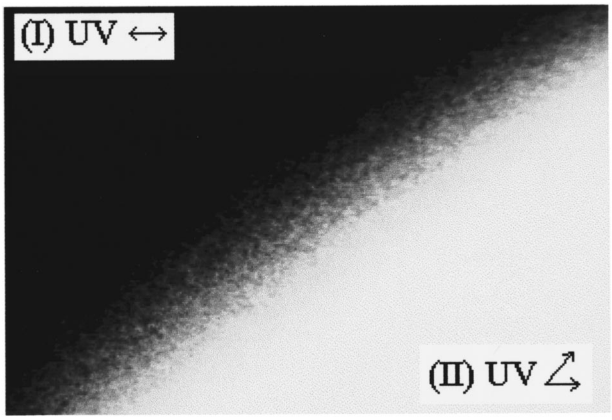

FIG. 5. Appearance of a homogeneously aligned multidomain cell between crossed polarizers. The polarization direction of first exposed LPUV coincides with the axis of one of the crossed polarizers. The polarization direction was at 45° to the polarizer axes. Dark (bright) region marked as I (II) represents one (two) LPUV exposure(s).

In conclusion, we have demonstrated a novel method for LC alignment using LPUV exposure during the imidization of polyimide. The preliminary results show that samples prepared by this method have better thermal stability and require less processing time. Research to generate pretilt angle using the *in situ* method is now underway. 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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