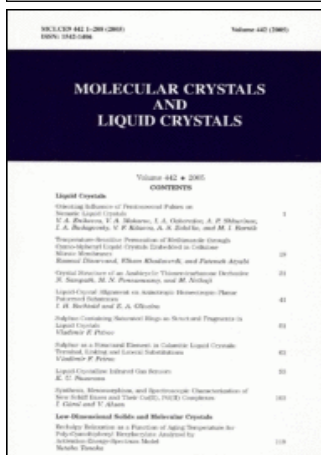


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# Molecular Crystals and Liquid Crystals

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## Multi-Domain Liquid Crystal Alignment by Micro-Contact Printed Polymer Layers

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*We proposed a patterning method of liquid crystal (LC) alignment layers for producing multi-domain LC structures. It was demonstrated that conventional LC alignment materials could be selectively patterned by controlling the surface wetting properties of a patterning material during micro-contact printing procedures. The proposed patterning method was particularly simple and, thus, easily applicable to several LC devices in enhancing or designing electro-optic properties by using multi-domain LC structures.*

**Keywords:** liquid crystal alignment; liquid crystal; micro-contact printing; multi-domain liquid crystal structure; patterned alignment layer; surface wetting

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## INTRODUCTION

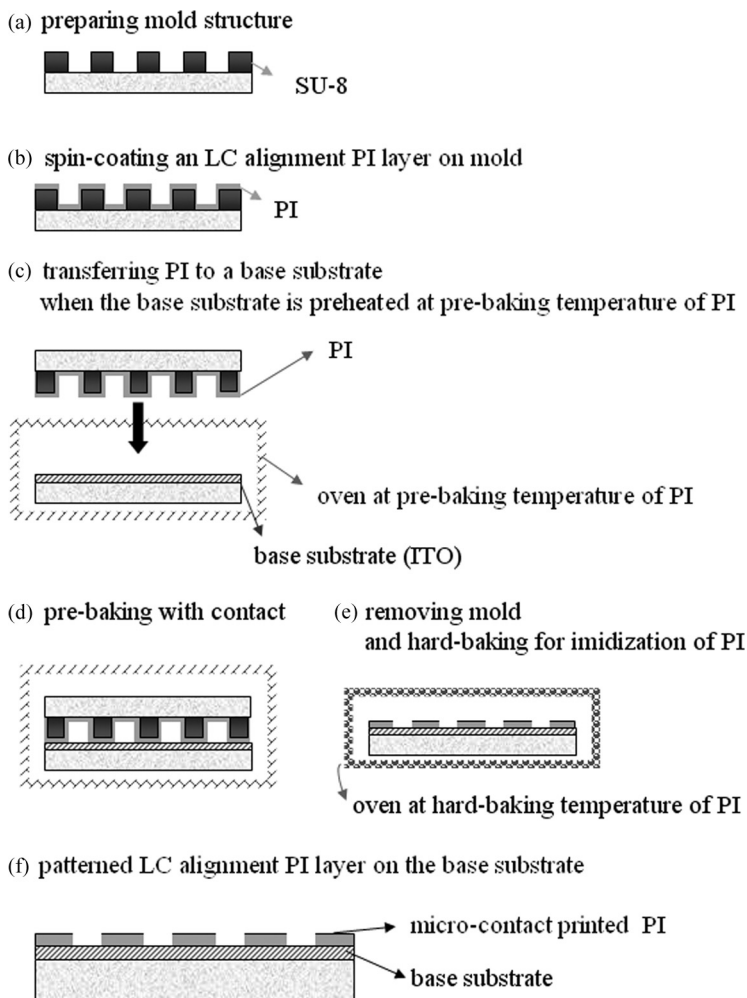
The electro-optic (EO) properties of liquid crystal (LC) devices highly depend on a LC geometry determined by surface alignment conditions. Recently, patterning methods of a LC alignment layer have attracted much attention for enhancing or manipulating EO properties of LC devices with multi-domain LC structures. A patterned alignment layers can solve conventional viewing angle limitation existing in mono-domain LC structures by adopting spatially distributed optic axes in multi-domain LC structures. In fabricating transmissive LCDs, the gray scale mismatch problems between the transmissive and reflective parts can be solved by designing different LC modes in the two parts [1]. LC orientations in a periodic pattern are essential feature in order to obtain desired EO properties when developing electrically controllable diffractive optical elements with LC materials.

To obtain multi-domain LC structures, several types of patterning method have been proposed. These include mechanical micro-rubbing methods by direct scribing with an atomic force microscope tip [2] or a metallic ball sphere [3,4] and photoalignment methods with a photo-sensitive materials through several steps of the photomasking process or holographic methods [5]. As a method for producing multi-domain LC structures with patterned multi-layers, photo-lithographic etching methods [6] were proposed. However, conventional multi-domain alignment methods were unattractive in that cumbersome several processing steps and/or long processing time were required. A recent research of a soft-lithographic patterning [7] using specific molecular binding events on a chemically modified surface showed relatively simple fabrication procedures. However, it seemed that stability and durability of LC anchoring had to be further examined.

In this paper, we propose a micro-contact printing method of LC alignment layers. By controlling pattern-transfer conditions such as wetting properties and baking temperatures of patterning polymers, patterned homeotropic or planar LC anchoring could be easily obtained with conventional polyimide (PI) materials. PIs are usually preferred as LC alignment agents due to their excellent thermal stability, chemical resistance, transparency in the visible spectral range, and reliability in LC anchoring.

## EXPERIMENTAL

The schematic illustrations of the micro-contact printing procedures for patterning PIs are shown in Figure 1. In our fabrication process, the alignment layer patterning was executed by single step of the



**FIGURE 1** Schematic illustrations of micro-contact printing procedures for patterning LC alignment PI layers.

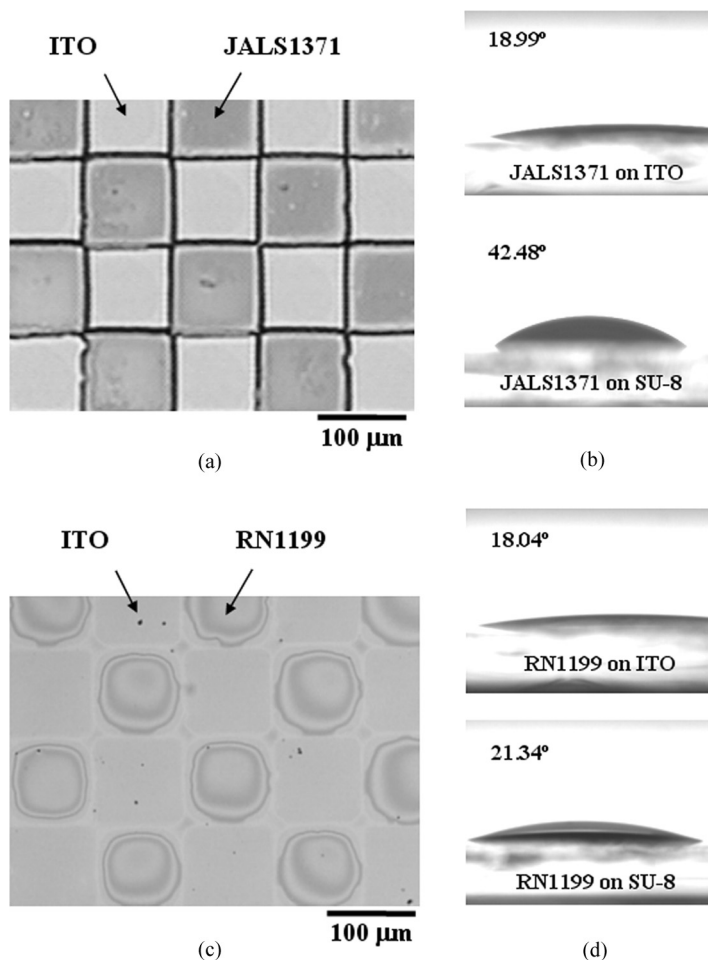
micro-contact printing without any etching process and any photo-mask process. First, an LC alignment agent of a PI was spin-coated on a patterned mold structure. Before transferring the PI to a base surface with the micro-contact printing, the base substrate was pre-heated to a pre-baking temperature of the PI, which enhanced adhesion of the patterning material to the base surface and precision of the resulting PI patterns. After placing the PI-coated mold structure

on the pre-heated base substrate, the contact was kept in the oven at the pre-baking temperature of the PI. During the first thermal treatment with contact, the solvents in the PI vaporized and the PI on the patterned mold surface was transferred to the base substrate. After removing the mold structure, the patterned PI was imidized by curing at a hard-baking temperature of the PI. To obtain uniform PI pattern, the imidization process should be executed without the contact of the mold because the imidization process enhances the adhesion of the PI to the mold surface. With the proposed method, the LC anchoring at the surface could be spatially modified in easy axis orientation, pretilt, and surface anchoring energy by selecting patterning PIs and the base surface conditions.

The patterned mold substrate was fabricated by a photolithographic method using negative photoresist of SU-8 (MicroChem). As patterning PI materials, commercially available PIs, AL1H659 (JSR Co.), RN1199 (Nissan Chemical Ind.), and JALS1371 (JSR Co.) were tested, where AL1H659 was a homeotropic LC alignment agent and both RN1199 and JALS1371 were planar LC alignment agents. As a base substrate, the bare ITO substrate was used in our experiment. The pre-baking of the PIs was executed with contact at 100°C for 30 minute. The hard-baking conditions of AL1H659, RN1199, JALS1371 were 220°C for 1 hour, 180°C for 1 hour, and 210°C for 40 minute, respectively.

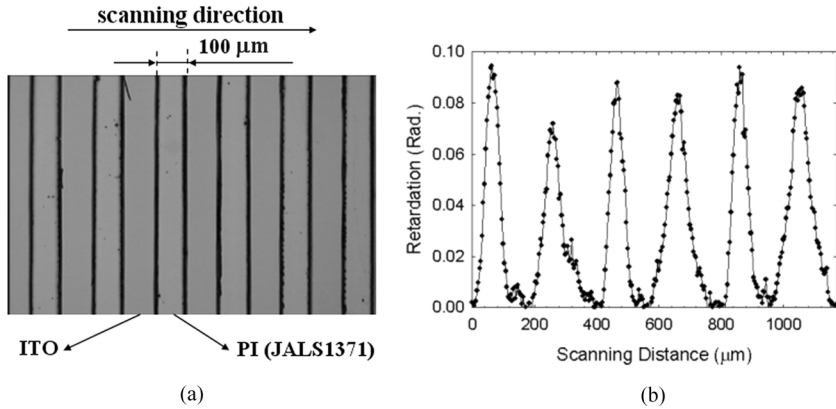
## RESULTS AND DISCUSSION

Figures 2 (a) and (c) show the patterned homogeneous LC alignment PIs on an ITO surface, which were observed by the optical microscopy in the reflective mode. In Figs. 2 (a) and (c), JALS1371 and RN1199 were used as the patterning PIs, respectively. The PI patterns were obtained by the SU-8 mold with a 100  $\mu\text{m}$  period of a check pattern. In case of the micro-contact printing of JALS1371, uniform PI pattern was obtained. Whereas, patterned result of RN1199 were highly non-uniform ones, where the thickness of the patterned PI layer showed much variation within each patterned area. These results originated in surface wetting difference of patterning materials between on the mold surface and on the base surface. Figures 2 (b) and (d) show the contact angles of JALS1371 and RN1199, respectively, on the ITO and the SU-8 mold surface. The contact angles were measured by observing equilibrium of sessile drop on the surfaces. The contact angles of both PIs showed similar values on the ITO surface but their wettability on the SU-8 surface showed much difference. The wettability of JALS1371 on the ITO surface was much higher than that



**FIGURE 2** Patterning of planar LC alignment PI layers on the ITO surface. (a) and (c) are the optical microscopic images of the patterned JALS1371 layer and the patterned RN1199 layer, respectively, on the ITO surfaces. (b) and (d) show the contact angles of JALS1371 and RN1199, respectively, on the ITO surface and the SU-8 surface.

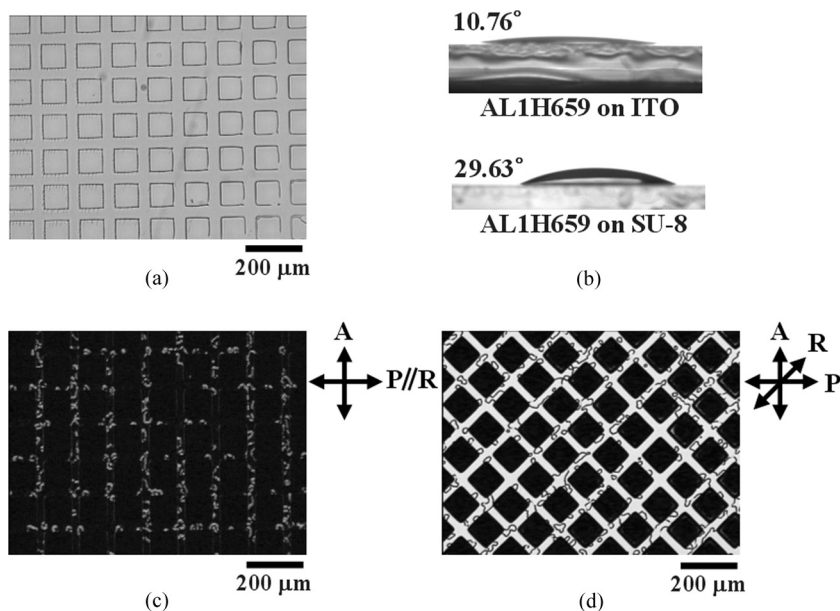
on the SU-8 surface. Therefore, JALS1371 on the patterned mold surface could be easily transferred to the base substrate. Whereas, RN1199 had no clear preference in wetting properties between on the mold surface and on the base surface, which resulted in the poor patterns as shown in Figure 2 (c). In case of RN1199, it was observed that much of PIs was remained on the mold surface after removing the contact.



**FIGURE 3** (a) Optical microscopic image of the patterned JALS1371 layer on the ITO surface where the rubbing direction is parallel to the line pattern. (b) Retardation variation of the patterned JALS1371 layer as a function of scanning distance.

Figure 3 (a) shows the optical microscopic image of a periodic line pattern (JALS1371) on the ITO surface, which was observed in the reflective mode. The patterned surface was unidirectionally rubbed along the direction of the line pattern. Thus, a homogeneously planar LC anchoring was periodically formed on the ITO surface, and weak birefringence was produced only in the areas with the patterned PI layer, which was due to the polymer chain ordering effect. The periodically patterned surface was probed by measuring variation of the optical retardation along a specified direction, as shown in Figure 3 (a). Figure 3 (b) shows the optical retardation variation as a function of scanning distance, where the polarization direction of the focused probing beam was  $45^\circ$  with respect to the rubbing direction. Since the spot size of the focused probing beam at the measuring distance was about  $100\ \mu\text{m}$ , half of the pattern periodicity, there was a spatially intensity-averaging effect in the birefringence measurement. Thus, the measured birefringence along the scanning direction showed an oscillatory behavior. However, note that the periodicity of the retardation precisely coincided with that of the mold structure.

Figure 4 (a) shows the optical microscopic image of the patterned homeotropic alignment PI (AL1H659) on the ITO substrate, where the periodically patterned areas were  $100 \times 100\ \mu\text{m}^2$  and the spacing between each pattern was  $40\ \mu\text{m}$ . AL1H659 was more wettable on the ITO surface than on the mold surface, as shown in Figure 4 (b). In this condition, we could get uniform homeotropic PI patterns as



**FIGURE 4** Patterning of homeotropic LC alignment PI (AL1H659) layer on the ITO surface. (a) Optical microscopic image of the patterned AL1H659 on the ITO surface. (b) shows the contact angles of AL1H659 on the ITO surface and the SU-8 surface. (c) and (d) are the polarizing optical microscopic images of the LC cell, where the LCs are aligned between the patterned homeotropic PI (AL1H659) layer and the non-patterned homeotropic PI (AL1H659) layer. **R**, **P**, and **A** denote the rubbing direction of the patterned substrate, and the transmission axes of the polarizers and the analyzers, respectively.

shown in Figure 4 (a). The patterned PI substrate was unidirectionally rubbed, and then it was assembled with the non-patterned PI (AL1H659) substrate. After filling nematic LC into the cavity, the LC textures, produced by the patterned PI substrate, was observed by the polarizing optical microscopy as shown in Figures 4 (c) and (d). In Figures 4 (c) and (d), **R**, **P**, and **A** denote the rubbing direction of the patterned substrate, and the transmission axes of the polarizers and the analyzers, respectively. On the patterned surfaces, the textures showed the complete dark states irrespective of cell rotation under the crossed polarizers, which meant that the LCs were homeotropically aligned with good uniformity. Whereas, on the non-patterned bare ITO surfaces, the LCs were aligned in a homeotropic-planar geometry and the retardation was produced by the LCs, as shown in Figures 4 (c) and (d).



## CONCLUSIONS

We proposed a patterning method for generating multi-domain LC structure, which could be realized with conventional LC alignment PIs. By controlling baking conditions during our micro-contacting printing procedures and using relative wetting difference of a patterning material between on the mold surface and the base surface, we could obtain uniformly and precisely patterned LC alignment layers on a bare ITO surface. Our micro-contact printing method can be simply achieved and the patterned PI surface shows stable multi-directional LC anchoring. Therefore, it is expected to be a very useful tool in enhancing or designing EO properties of LC-based devices with multi-domain LC structures.

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