

Molecular orientation of a photoreactive liquid crystalline polymer induced by thermal nanoimprinting and graphoepitaxy



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ABSTRACT

Molecular orientation in photoreactive liquid crystals (LCs) can be induced by linearly polarized ultraviolet light and heat. Thermal nanoimprinting has similarities to graphoepitaxy, including using patterned substrates and heating. Diffraction efficiencies were measured to compare the molecular orientation of the photoreactive LC polymer P6CAM induced by thermal nanoimprinting, with that induced by graphoepitaxy. P6CAM was reoriented by graphoepitaxy, but the degree of orientation was much smaller than that induced by thermal nanoimprinting.

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1. Introduction

Liquid crystals (LCs) are widely used in optical devices, and LC molecules are generally reoriented via a rubbing process. Recently, a photo-induced orientation process for photoreactive LCs was reported [1–10]. Kawatsuki and coauthors reported a polymethacrylate derivative with a side chain containing a hexamethylene spacer group terminated with 4-oxycinnamic acid (P6CAM), and used it as a photoreactive LC [11,12]. P6CAM dimerizes and exhibits LC characteristics, and the dimers exhibit axis-selective photo-reactivity. P6CAM can be reoriented by linearly polarized ultraviolet (LPUV) irradiation and heating.

Nanoimprinting can be used to fabricate nanostructured devices with high throughput, low cost, and high accuracy [13–23]. Polymethylmethacrylate, polystyrene, UV-curable resins, and spin-on-glasses are typical nanoimprinting resins for applying resist masks. The patterning of functional materials by nanoimprinting has also been reported. Aryal and coauthors reported that the electrical conductivity of the organic semiconductor poly-3-hexylthiophene was improved by thermal nanoimprinting [24]. Chiu and coauthors reported that the polymerizable LC oligomer was reoriented by UV nanoimprinting [25]. Nanoimprinting is an etch-free technique that can be used to fabricate nanostructures

on functional materials, in contrast to traditional lithography. Damage to the quality of the functional material is therefore much less than that caused by traditional lithography. Functional augmentation and new features can potentially be induced by the functional materials nanostructure. We reported that P6CAM was reoriented by thermal nanoimprinting, in the absence of LPUV irradiation [26]. This study involved a 2- μm positive tone line and space (L&S) pattern (4- μm pitch) mold, so the pattern size was much larger than a P6CAM molecule. After thermal nanoimprinting, the imprinted P6CAM pattern was observed by polarized optical microscopy (POM) under crossed Nicols, and the molecular orientation was determined by optical measurement. P6CAM was reoriented parallel to the imprinted line pattern, while P6CAM in imprinted non-patterned areas maintained a random orientation. Thus, the pattern fabricated by thermal nanoimprinting induced the molecular reorientation of P6CAM.

Graphoepitaxy usually refers to the varying orientation of crystals [27] or block copolymer assemblies [28], induced by relief features of the substrate. The relief features can be much larger than the lattice parameter of the orientated material, so graphoepitaxy can be used to induce molecular orientation. Thermal nanoimprinting has similarities to graphoepitaxy, such as using patterned substrates and heating. However, thermal nanoimprinting also includes a pressing process. In the current study, we compared the molecular orientation of P6CAM induced by thermal nanoimprinting with that induced by graphoepitaxy.

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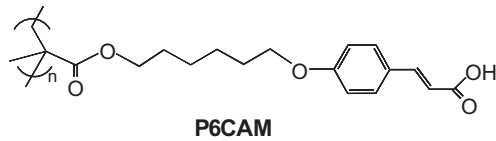


Fig. 1. Chemical structure of the photoreactive crystalline polymer P6CAM.

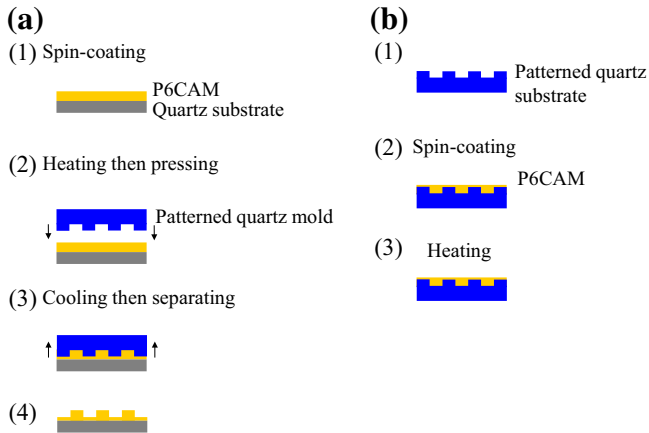


Fig. 2. (a) Thermal nanoimprinting and (b) graphoepitaxy processes for P6CAM.

2. Comparison between P6CAM orientation induced by thermal nanoimprinting and graphoepitaxy

2.1. Sample fabrication

P6CAM was used as a functional material, and was prepared as previously described [11]. Fig. 1 shows the chemical structure of

P6CAM. A positive tone L&S pattern was fabricated on a quartz substrate by electron beam lithography and reactive ion etching. The L&S widths were 2 μm , and the pattern height was 200 nm. Fig. 2(a) and (b) illustrates the thermal nanoimprinting and graphoepitaxy processes for P6CAM, respectively. Thermal nanoimprinting was carried out using a patterned quartz mold on P6CAM. The P6CAM liquid crystalline temperature range is about 140–190 $^{\circ}\text{C}$. Fig. 2(a) shows that the process was performed as follows. (1) P6CAM was spin-coated on a quartz substrate. (2) The mold and substrate were heated to 165 $^{\circ}\text{C}$, after which the mold was pressed into the P6CAM. The mold was pre-coated with a thin polydimethylsiloxane (PDMS) anti-sticking layer [29]. The imprinting pressure and time were 15 MPa and 2 min, respectively. (3) After cooling, the mold was removed from the P6CAM substrate. Graphoepitaxy is a comparatively simple process. Fig. 2(b) shows that P6CAM was spin-coated on a patterned quartz substrate, and heated at 165 $^{\circ}\text{C}$ for 10 min.

The molecular orientation of P6CAM was investigated by measuring the diffraction efficiency using linearly polarized (LP) 633 nm light, at angles of incidence from 0 to 180 $^{\circ}$. The diffraction efficiency is defined as the ratio of diffracted to incident light intensity. Fig. 3(a) and (b) shows the optical measurement setup and orientation of the LP incident light and L&S pattern, respectively. The angle between the incident LP light and L&S pattern is θ . Rotation angles of 0 and 90 $^{\circ}$ indicate that the incident LP light direction is parallel and perpendicular to the L&S pattern, respectively. The ± 1 st-order diffraction efficiency is at a maximum, when the P6CAM orientation and direction of incident LP light are the same. A patterned quartz substrate was used in the graphoepitaxy process. The diffraction efficiency of the 2- μm L&S patterned quartz substrate is shown in Fig. 3(c). The diffraction efficiency did not change upon rotating the incident LP light. Thus, the dif-

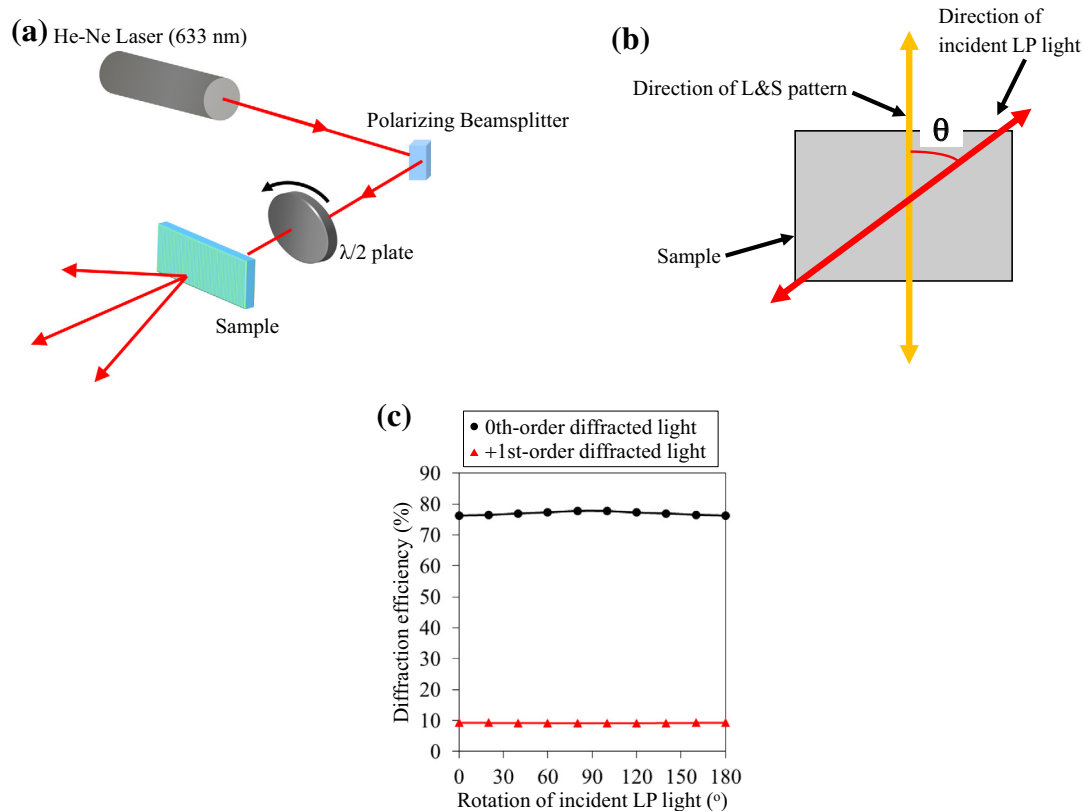


Fig. 3. (a) Optical measurement setup. (b) Relationship between incident LP light direction and L&S pattern during optical measurement. (c) Diffraction efficiency of positive tone L&S patterned quartz substrate. The L&S widths were 2 μm , and the pattern height was 200 nm.

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