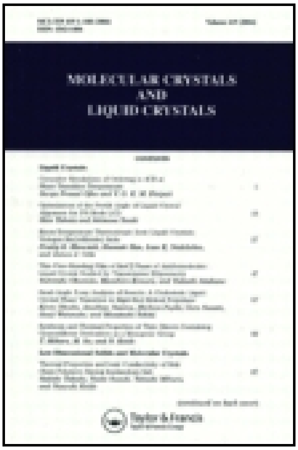


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Planar Alignment of Columnar Liquid Crystals in Microgroove Structures

Kazuki Tokuoka [a], Hiroyuki Yoshida [a], Yasuo Miyake [a b], Chee Heng Lee [a], Yusuke Miura [a], Satoshi Suzuki [a], Akihiko Fujii [a], Yo Shimizu [b] & Masanori Ozaki [a]

[a] Department of Electrical, Electronic and Information Engineering, Osaka University, Osaka, Japan

[b] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Kansai Center, Osaka, Japan

Version of record first published: 05 Oct 2009

Mol. Cryst. Liq. Cryst., Vol. 510, pp. 126/[1260]–133/[1267], 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903060185

Planar Alignment of Columnar Liquid Crystals in Microgroove Structures

Kazuki Tokuoka[1], Hiroyuki Yoshida[1], Yasuo Miyake[1,2], Chee Heng Lee[1], Yusuke Miura[1], Satoshi Suzuki[1], Akihiko Fujii[1], Yo Shimizu[2], and Masanori Ozaki[1]
[1]Department of Electrical, Electronic and Information Engineering, Osaka University, Osaka, Japan
[2]Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Kansai Center, Osaka, Japan

Planar alignment of columnar liquid crystals was achieved in microgroove structures fabricated by a direct laser lithography using two photon polymerization. A liquid crystalline material exhibiting the columnar phase was sandwiched between a substrate with microgrooves and an untreated glass substrate, and the orientation characteristics were investigated with a polarizing optical microscope. A uniform uniaxial alignment was observed in the microgrooves, and the measurement of the optical birefringence indicated that the columnar director aligned perpendicularly to the grooves.

Keywords: columnar liquid crystal; microgroove; planar alignment

INTRODUCTION

Columnar liquid crystals have potential as organic semiconductors for electronic devices due to highly mobile charge carriers along the columnar axis (director) [1]. In addition, self-organization is a desirable nature for the device application because uniform alignment of molecules can be easily obtained over a large area.

This work was partly supported by KAKENHI (Grant-in-Aid for Scientific Research) given by the Ministry of Education, Science, Sports and Culture.

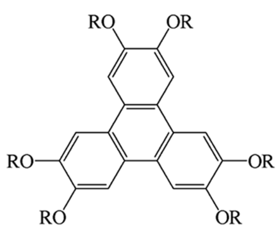
Address correspondence to Kazuki Tokuoka, Department of Electrical, Electronic and Information Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: ktokuoka@opal.eei.eng.osaka-u.ac.jp

In order to fabricate highly efficient devices based on columnar liquid crystals, alignment control of the columns is essential: homeotropic alignment (columns orient perpendicular to the substrate) is desirable for solar cells, and planar alignment (columns orient parallel to the substrate) is desirable for field effect transistors [2]. Until now, it has been reported that the introduction of fluoroalkylated chains onto the peripheral parts of a triphenylene mesogen leads to a strong tendency for homeotropic alignment [3]. On the other hand, planar alignment has been achieved using several techniques such as a zone-casting [4] and polytetrafluoroethylene coating which is so-called a friction-transfer technique [5]. However, a novel technique to obtain uniform planar alignment is still needed to realize highly efficient organic transistors.

Here, we present a novel method to obtain planar alignment in columnar liquid crystals: we show that columnar liquid crystals introduced in microgroove structures fabricated by direct laser lithography (DLL) exhibit a planar orientation with the columnar axis being perpendicular to the microgrooves.

MATERIALS

The material used to fabricate microgrooves comprised of a colorless, urethane-based ultraviolet (UV)-curable photopolymer (NOA61, Norland), with 0.1 wt% of bis(2,4,6-trimethylbenzoy) phenylphosphine oxide (Irgacure819, Ciba) for enhancing the absorption at $\lambda = 400$ nm, and 0.1 wt% of 4-(dicyanomethylene)-2-methyl-6-(4-dimethyl aminostyryl)-4*H*-pyran (DCM, Exciton) dye for observation purpose. NOA 61 was selected due to its fast curing time, good adhesion and chemical stability.



C6OTP : R=C_6H_{13}
C7(F4H3)OTP : R=$C_3H_6C_4F_9$

compound	phase transition temperature / °C
C6OTP	Cr 69 Colh 99 Iso
C7(F3H3)OTP	Cr 120 Colh 157 Iso

Cr: crystal, Colh: hexagonal columnar phase,
Iso: isotropic liquid

FIGURE 1 Chemical structures and phase transition temperature of C6OTP and C7(F4H3)OTP.

The liquid crystalline materials used were 2,3,6,7,10,11-hexahexyloxy-teiphenylene (C6OTP) and C7(F4H3)OTP. C7(F4H3)OTP is a triphenlene based compound with fluoroalkylated chains on the peripheral parts. Both compounds exhibit the hexagonal columnar phase: the chemical structure and phase sequence of each material is shown in Fig. 1.

EXPERIMENTAL

The experimental setup for the fabrication process is schematically illustrated in Figure 2(a). Fabrication was performed in a dark room to avoid unnecessary curing of the materials. DLL was carried out using a confocal laser scanning microscope (CLSM) system (Carl Zeiss, LSM 510). The cover glass with the spin-coated materials was positioned on the stage of the CLSM, and then irradiated with 100fs pulses of a focused Ti:sapphire laser (Spectra Physics, Maitai) at $\lambda = 800\,\text{nm}$ and repetition rate of 80 MHz. The laser was focused by a high numerical aperture oil-immersion objective lens (63×, N.A = 1.4). A position of the focused spot on the sample was controlled by a galvanometer to scan arbitrarily within a maximum scanning area ($146.2 \times 146.2\,\mu m^2$). Irradiated by the focused laser, reaction of photopolymerization occurs only in the vicinity of the focal point under the process of two photon excitation due to the high photon density in that region. Thus, it is possible to fabricate miniature groove structures with high resolution. DLL was performed under laser intensities varying between $2 \sim 6\,\text{MW/cm}^2$ and scan speed of 179 μs/μm. After irradiating

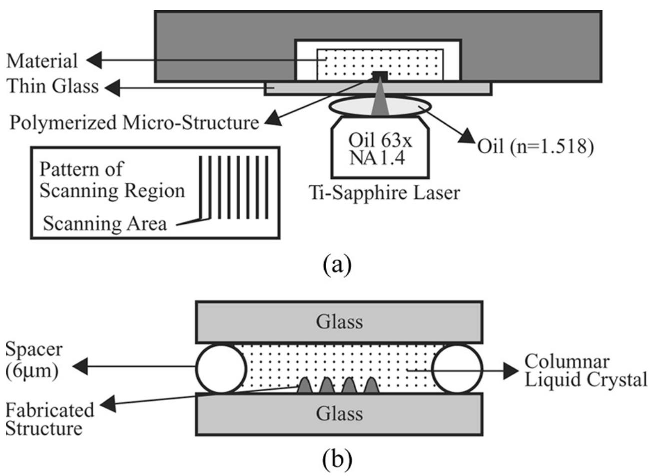


FIGURE 2 Schematic diagram of the experimental setup.

the laser, the uncured material was removed by rinsing in acetone for 10 sec and ethanol for 30 sec, so that only the cured microgroove structures were left on the cover glass surface. The fabricated microgrooves were investigated with an atomic force microscope (AFM) (KEYENCE, VN-8000).

The structure of the liquid crystal cell is shown in Figure 2(b). The 6 μm-cell was comprised of a substrate with the microgrooves and an untreated glass substrate. The columnar liquid crystal (C6OTP or C7(F4H3)OTP) was infiltrated into the cell by first heating to the isotropic phase, and then cooling the sample to the columnar mesophase. The alignment characteristics were investigated under crossed Nicols on a polarization optical microscope (POM) (Nikon, Eclipse E600-POL). The retardation and the optical birefringence were measured using a Berek compensator.

RESULTS AND DISCUSSION

Figure 3 shows the AFM image of microgroove structure with the width of 1.5 μm and the height of 1.5 μm. The alignment properties were investigated in the cell with this groove structure. Figure 4(a) and (b) are the POM images of the cell after infiltrating C6OTP. When the groove direction was parallel to either the polarizer or the analyzer, the region with the microgroove structure appeared dark (Fig. 4(a)). The region with the grooves appeared bright (Fig. 4(b)), when the stage was rotated by 45°. This indicates that planar uniaxial alignment was obtained in the microgrooves. Moreover, the evaluation of the optical axis using a Berek compensator indicated the direction of the columnar axis to be perpendicular to the microgroove, as shown

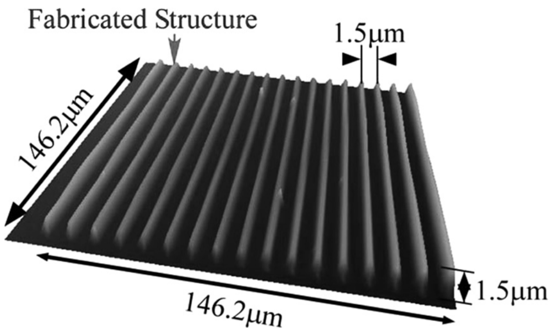


FIGURE 3 AFM image of microgroove structure.

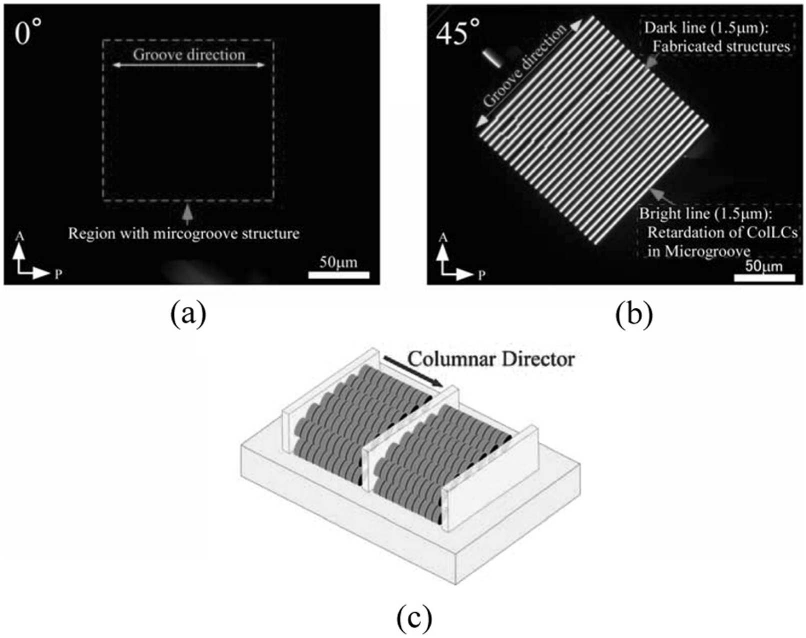


FIGURE 4 POM images of aligned columnar liquid crystal (C6OTP) in microgroove strucutures (a) extinction position (the groove direction was parallel to the polarizer), (b) after rotation of the sample on the stage by 45°, and (c) schematic model of aligned columnar liquid crystals in microgrooves.

in schematic model of Figure 4(c). In addition, this uniaxial alignment was also observed in microgroove structure (width 1 μm and height 2 μm) for another columnar liquid crystal, C7(F4H3)OTP (Fig. 5).

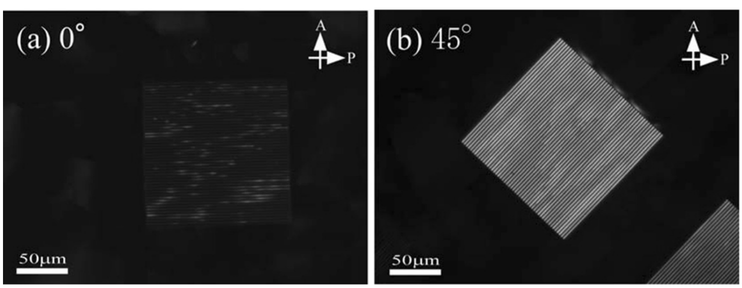


FIGURE 5 POM images of aligned columnar liquid crystal (C7(F4H3)OTP) in microgroove strucutures (a) extinction position (the groove direction was parallel to the polarizer), and (b) after rotation of the sample on the stage by 45°.

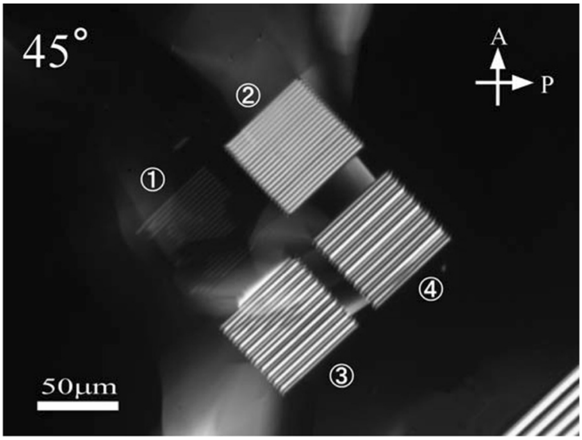


FIGURE 6 POM image of the effect of varying microgroove height (The groove height is ① 1 μm, ② 3 μm, ③ 4 μm, and ④ 5 μm).

Next, the effect of alignment properties by varying microgroove height was investigated. The groove height was varied between 1 μm, 3 μm, 4 μm, and 5 μm (the width was 1.5 μm). Figure 6 shows the POM image of four square regions with different groove height. The retardation and the birefringence in these regions are shown in Table 1. The birefringence (Δn) was evaluated from the retardation ($R = \Delta nd$) measured by a Berek compensator and the groove height (d) measured with an AFM. The retardation increased as growing the height between 3 μm, 4 μm, and 5 μm, although that of the 1 μm-height could not be measured because the value is too small. On the other hand, the birefringence is approximately the same irrespective of the groove height. These observations suggest that

TABLE 1 Effect of Varying Microgroove Height (d): Retardation ($|\Delta n|d$) and Birefringence ($|\Delta n|$)

Number of Groove structure	Groove height d	Retardation ($=|\Delta n|d$)	Birefringence $|\Delta n|$
①	1.0 μm	×	×
②	3.0 μm	254 nm	0.085
③	4.0 μm	347 nm	0.087
④	5.0 μm	485 nm	0.097

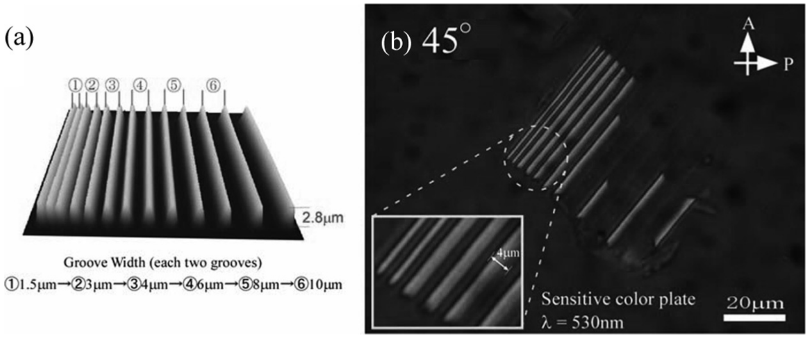


FIGURE 7 Effect of varying microgroove width (a) AFM image, and (b) POM image with sensitive color plate ($\lambda = 530\,nm$).

columnar liquid crystals align parallel to the glass substrate only in the microgrooves.

The effect of varying microgroove width was also investigated. Figure 7(a) shows the AFM image of the microgroove structure used for the measurement whose width was 1.5 μm, 3 μm, 4 μm, 6 μm, 8 μm, and 10 μm (the height was 2.8 μm). Figure 7(b) shows the POM image with a sensitive color plate ($\lambda = 530\,nm$). When the width was less than 3 μm, a uniform uniaxial alignment was observed. However when the width was larger than 3 μm, the retardation gradually decreased at distances far from the edge. Considering that the columns tend to align perpendicular to the substrate between untreated glasses [2], we believe that the columns gradually tilted and became homeotropic at regions far from the groove edge, as shown in Figure 8.

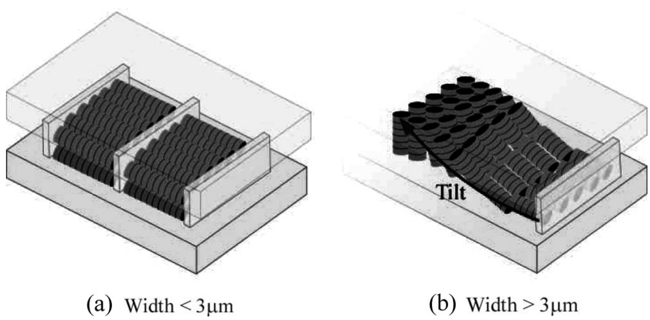


FIGURE 8 Schematic model of aligned columnar liquid crystals in microgroove structures.

CONCLUSION

In conclusion, planar uniaxial alignment of columnar liquid crystals (columns orient parallel to the glass substrate) was obtained in microgroove structures fabricated by DLL method via two photon polymerization. The columnar axis was perpendicular to the microgrooves. When the groove width was less than 3 μm, a uniform uniaxial alignment was observed. However, when the width was larger than 3 μm, a uniform uniaxial alignment was not obtained. It is considered that the columns gradually tilts and becomes homeotropic at regions far from the groove edge.

REFERENCES

[1] Adam, D., Schuhmacher, P., Simmerer, J., Häussling, L., Siemensmeyer, K., Etzbach, K. H., Ringsdorf, H., & Haarer, D. (1994). *Nature*, *371*, 141.
[2] Sergeyev, S., Pisula, W., & Geerts, Y. H. (2007). *Chem. Soc. Rev.*, *36*, 1902.
[3] Terasawa, N., Monobe, H., Kiyohara, K., & Shimizu, Y. (2003). *Chem. Commun.*, 1678.
[4] Pisula, W., Menon, A., Stepputat, M., Lieberwirth, I., Kolb, U., Tracz, A., Sirringhaus, H., Pakula, T., & Müllen, K. (2005). *Adv. Mater.*, *17*, 684.
[5] Craats, A. M., Stutzmann, N., Bunk, O., Nielsen, M. M., Watson, M., Müllen, K., Chanzy, H. D., Sirringhaus, H., & Friend, R. H. (2003). *Adv. Mater.*, *15*, 495.