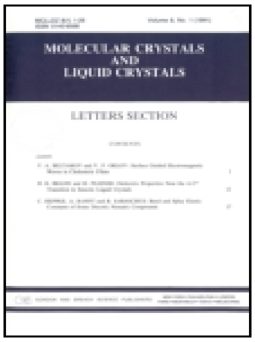

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# Alignment of columnar phase confined in polydimethylsiloxane microchannels

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**ABSTRACT**
The alignment of a discotic liquid crystal confined in polydimethylsiloxane (PDMS) channels with a rectangular cross-section is studied. The microchannels were produced in PDMS using the mold-replica technique. In the PDMS channels, the disc-like molecules of the disogen were found to adopt an edge-on anchoring at the PDMS surface, and macroscopically, the discogen layer is planarly aligned. Using Newton colour scale technique it was revealed that discotic columns were aligned parallel to the channels.

**KEYWORDS**
Columnar phase; discotic liquid crystal alignment; micro-replica; polymer walls; polydimethylsiloxane confinement

## 1. Introduction

Discotic molecules possess manifold of unique properties that are profoundly fascinating as well as highly useful. The central conjugated core of the molecules allows the discotic molecules to stack face to face and further pile into columns. The construction of discotic molecular assemblies of $\pi$-conjugated systems provides an excellent means to construct conducting wires of electronic components in the nano meter range. When the discotic molecules assemble into an organized columnar phase, the one dimensional (1D) charge carrier transportation [1–3], which is particularly useful for a wide range of organic electronic devices that are prefer 1D conduction [4], may be allowed in the DLC, and thus the DLCs are thought to be candidates for molecular electronics. The device applications of DLCs rely on the attainment of the required alignment of columnar phases. An effective control of the molecular stacking and the orientation of the discotic columns to produce an appropriate molecular alignment is a crucial factor for the operation and performance of LC devices.

The discotic molecules are anisotropic with its dimension in the diameter much larger than its dimension in thickness. The molecular axis of a discotic molecule is defined as the symmetric axis normal to the plane of the discotic molecule. In a mesophase, the discotic molecules tend to align parallel to the director $\mathbf{n}(\mathbf{r})$, the unit vector that describes the local average orientation of the molecular axes at position $\mathbf{r}$ [5]. When a DLC is confined between two substrates of solid state, two basic molecular anchoring can be found: the face-on anchoring, in which the disc-like molecules reside on a substrate with their plane of the molecule (i.e. the "face") towards the substrate, and the edge-on anchoring, in which the molecules anchored with their

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edges in contacting with the substrates. If all molecules at the surface are orient in one direction and create a unique director **n** and the respective surface anchoring can smoothly evolve into the bulk, either the homeotropic alignment, in which the director **n** orients normal to the bounding surfaces, or planar alignment, in which **n** is confined to a specific direction within the plane parallel to the bounding surfaces, is formed.

Over the years, considerable efforts have been made and several techniques such as Langmuir-Blodgett deposition [6], Zone-casting [7, 8], the use of magnetic field [9] and laser irradiation [10, 11] have been proposed to realize the orientational control of the stack disc-like molecules and the discotic columns. However, a practical technique that can be used for the attainment of a molecular alignment of the DLCs that satisfies commercial device requirement has not been achieved. The primary reason for this is an ambiguous understanding on the mechanism of the self-assembly of discotic molecules and how the aggregated discotic molecules assemble into an ordered structure. A lack in the knowledge on the surface properties of the substrates that used to confine DLCs and the interactions between discotic molecules and the surfaces is also a major missing link.

For quite a long period the behaviour of nematic LC in confined geometries has been a research topic of great interest for both basic scientific and technological reasons. It was shown that proper energy barriers may be built up by creating lateral confinement by the provision of a structured surface morphology on one or both of the bounding surfaces thus separating the otherwise continuous LC layer into square wells [12–14] or into patterned channels [15, 16]. It has also been demonstrated that high quality alignment of DLCs can be achieved within microchannels [17, 18]. In this context, two issues are taken into account: a material whose chemicophysical properties can deliver a suitable function for molecular anchoring, and an effective technique that can be used to manipulate a right structure into the material. In most of the mentioned studies, trenches and/or channels in micro or nano size were produced in a SU8 substrate using E-beam [18] or photo-lithography [16].

Our attention was caught by polydimethylsiloxane (PDMS), a polymeric organosilicon compound, for its easy processing nature and good chemicophysical properties. This silicon-based polymer has been used as a replica of the microstructure of a surface [19, 20] that has been found to have a wide range of applications from microfluidic systems, [21] bio-medical applications, [22, 23] to optical devices [24]. In thin-film form, PDMS possesses a very low surface free energy, and was found to be capable of supporting vertical alignment of the calamitic liquid crystals [16]. Motivating by the success of the use of PDMS in calamitic LC alignment, we attempted to control disc-like molecule stacking and achieve macroscopic alignment of a DLC in a PDMS confinement. Recently, we confined a discogen in PDMS micro-channels with a rectangular cross-section, and observed molecular orientation of the DLC confined in the channels. We here demonstrate that microchannels can be produced in PDMS using mold-replica technique. The disc-like molecules adopt the edge-on anchoring at the PDMS surface, and a planar alignment of the discogen layer is achieved in the PDMS channels with discotic columns orienting parallel to the channels.

## 2. Experimental

PDMS thin layers consisted of microchannels were produced using a micro-replica molding technique. The polymer precursor used for the replica was Sylgard 184 (Dow Corning), which is a two-component silicone elastomer supplied in two separate parts, a base resin and a curing agent. Typically, a 10:1 ration of base to curing agent was used in our studies. The mixture was degassed over 1 hr in a vacuum chamber.

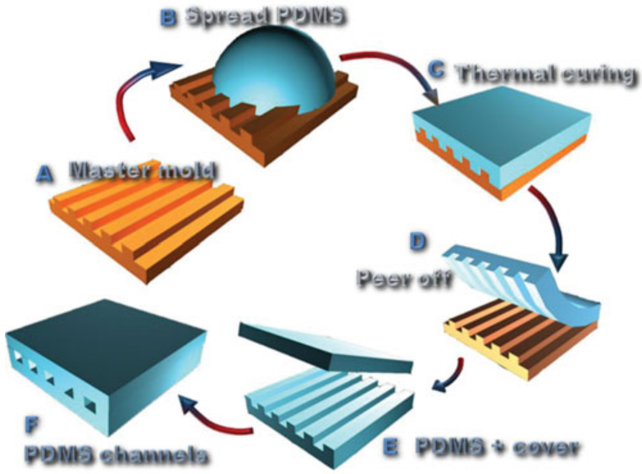

**Figure 1.** Schematic illustrating the main procedures for producing PDMS micro-channels: (A) Fabricate a master mould with desired surface pattern. (B) Spread PDMS precursor onto the mould. (C) Thermally cure the precursor. (D) Peer the PDMS form the mould. (E) Cover the patterned PDMS with a flat PDMS plate, and (F) to create microchannels in the resultant PDMS.

The master molds were produced using standard photolithographic fabrication procedures. A negative photoresist resin SU8-GM1060 (Gersteltech Sarl) was spun onto an optical-flat glass slide of $15 \times 15$ mm$^2$, and then soft-baked at 60°C for about 15 min to remove the solvent by evaporation. The baked photoresist layer was masked, exposed to 365 nm ultraviolet (UV), and then developed. The portion of photoresist that was exposed to the UV irradiation became insoluble to the photoresist developer, and will remain on the substrate, whereas the unexposed portion of the photoresist was dissolved by the developer and washed away. The pattern of the photoresist remained on the substrate was determined by the mask pattern. In the present study, masks comprising parallel UV-transparent stripes with 10 $\mu$m pitch and 50% duty cycle were used. Therefore, the resultant master comprised parallel grooves. As the unexposed part of the photoresist layer is completely washed away, the depth of the grooves is equal to the thickness of the photoresist layer, and controlled by the speed of the spin-coater.

The procedure of the micro-replica molding process is shown schematically in Fig. 1. The PDMS precursor was cast onto the mold, and was thermally cured at 130°C for 1 hr. After thermal curing, the PDMS thin film was peered from the mold. As a result of the replica-molding process, the surface pattern of the master is transferred onto the PDMS replica. A cell, which consists of micro-channels with a rectangular cross section (c.f. Fig. 1), was constructed by covering the PDMS film bearing the micro-grooves with a piece of PDMS.

The discogen used was 1–3,4-bis(octyloxy)phenyl)-2-(3-(3,4-bis(octyloxy)phenyl)-1H-pyrazol-5-yl)ethanon, a derivative of heterocyclic pyrazoles labelled with OPE10 for convenience. The chemical structures and the phase sequence are displayed in Figure 2. The compound exhibits hexagonal columnar phase (Col$_h$) within a moderate temperature range ($<$ 100°C). Details of the compound were provided elsewhere [25]. The discogen was injected into the micro-channels by capillary action at 105°C, about 10°C above the isotropic-Col$_h$ transition temperature. After filling, the device was cooled at a rate 0.3°C/min to room temperature. The molecular alignment of the LC in the sample cells was examined using a polarizing optical microscope (POM) (ZEISS, Axioskop40).

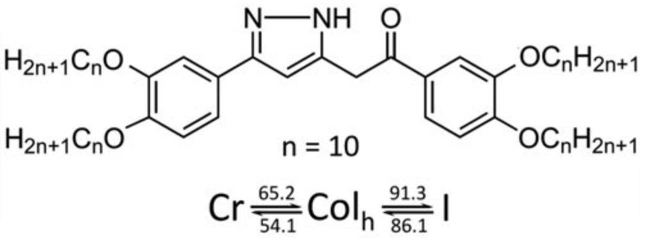

**Figure 2.** Chemical structure and phase sequence of discogen OPE10.

## 3. Results and discussions

In thin film form, PDSM exhibits a high hydrophobicity and possesses a low surface free energy. Our previous studies indicate that when curing the precursor at 130°C, the PDMS film can reach a stable energetic state (with a surface free energy of 24 mJ/m$^2$) in 1 hr (see Fig. 3). The curing temperature dependent surface free energy is believed to result from an incomplete conversion of precursor and/or different morphologies of the resultant PDMS thin films. Therefore, in the present study, all PDMS samples were cured at a temperature of 130°C for 1 hr in an oven. The low energy PDMS surface has been proven to be capable of supporting vertical anchoring for calamitic liquid crystal molecules [14]. However, discotic molecules are unique with their idiographic characteristics. The effect of PDMS on DLC alignment needs to be examined. For this purpose, empty cells were constructed by putting two PDMS-coated substrates together, with polymer surface facing each other. The gap of the cells was defined using 10 $\mu$m spacers. Prior to the cell preparation, no further process had been carried out for the PDMS surface after the thermal curing process. OPE10 was then heated to 105°C, where the discogen was in isotropic state, and allowed to be driven into the cells by capillary action. In most samples made using as-treated substrates, OPE10 layers exhibited fan shape textures in the cells (Fig. 4) indicating that the molecules adopted an edge-on anchoring [26]. The optical texture of the DLC layer also showed that a molecular alignment, in which all disc-like molecules orient in a unique direction, was not achieved. This is reasonable since there is

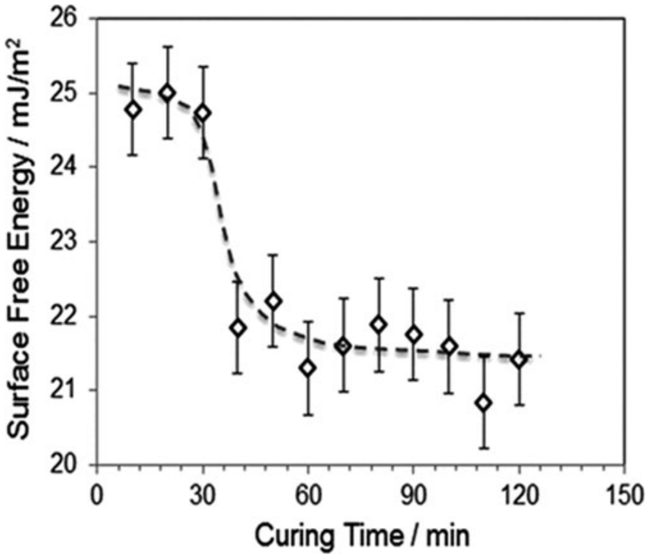

**Figure 3.** Surface free energy of PDMS film against curing time.

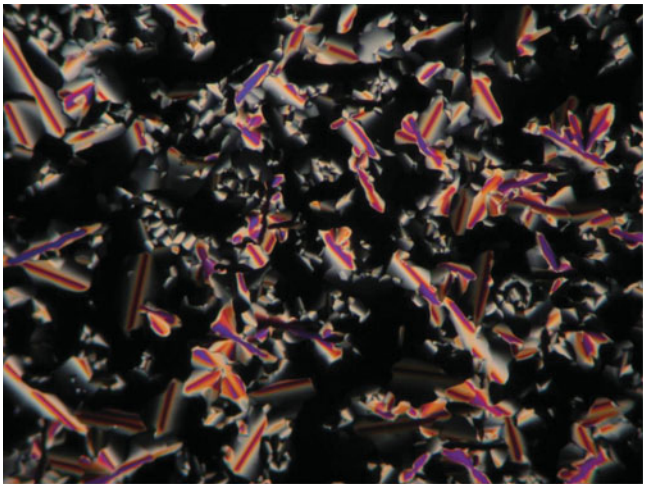

**Figure 4.** Optical texture of discogen OPE10 sandwiched between flat PDMS substrates. The thickness of the discogen layer is 10 $\mu$m.

more than one easy direction at the uniform and flat PDMS surface and the assemblage of the easy directions creates certain favourite orientations of the columnar phase at the surface. For our present study, the attention is not on whether the DLC is aligned, rather, it is important to learn that the molecules are adopting edge-on anchoring at the PDMS surface.

A topographic change in the surface will change the manifold of the surface energy. A theoretical description of the variation of the energetic state at the surface will involve intensive computation. In the present study, we kept the width of the channels fixing at 10 $\mu$m, and allow the depth of channel in the PDMS to vary. When the sample was rotated in the polarizing microscope, the light transmission was found to vary periodically and can be described as [27]

$$I = I_o \sin^2(2\phi)\sin^2(\Gamma/2) \tag{1}$$

where $\phi$ is the azimuthal angle the channels made against the axis of the polarizer, $\Gamma$ is the phase difference between the extraordinary and the ordinary light beams generated by the propagation through the sample. Figure 5. shows the photomicrographs of a sample consisted of 8.2 $\mu$m deep channels when the channels were aligned parallel to and to make 45° against the axis of the polarizer of the microscope, respectively. The azimuthal change in the optical transmission indicates that the discogen in the channels are aligned and forms a uniaxial continuum, with its optical axis parallel to the substrate surface, i.e. the discogen is in planar alignment. Although the planar alignment of the discogen in the channels was confirmed, we were unable to determine in which direction that the discotic columns orient since the optical states of the discogen layer for the discotic columns orient parallel to and perpendicular to the channels, respectively, are not distinguishable. That is to say, the discogen layer with either the two orientational directions as mentioned will exhibit the same optical appearances shown in Fig. 5.

We determined the orientation direction of the discotic columns in the channels using the Newton colour scale [28]. A de Sénarmont phase compensator (with 550 nm retardation) was used for the measurement. When the slow axis of the compensator was aligned parallel to the slow axis of the discotic columns, the sample appears blue due to an increase in the retardation, as illustrated in Fig. 6a; whereas the sample appears yellowish-red because of a

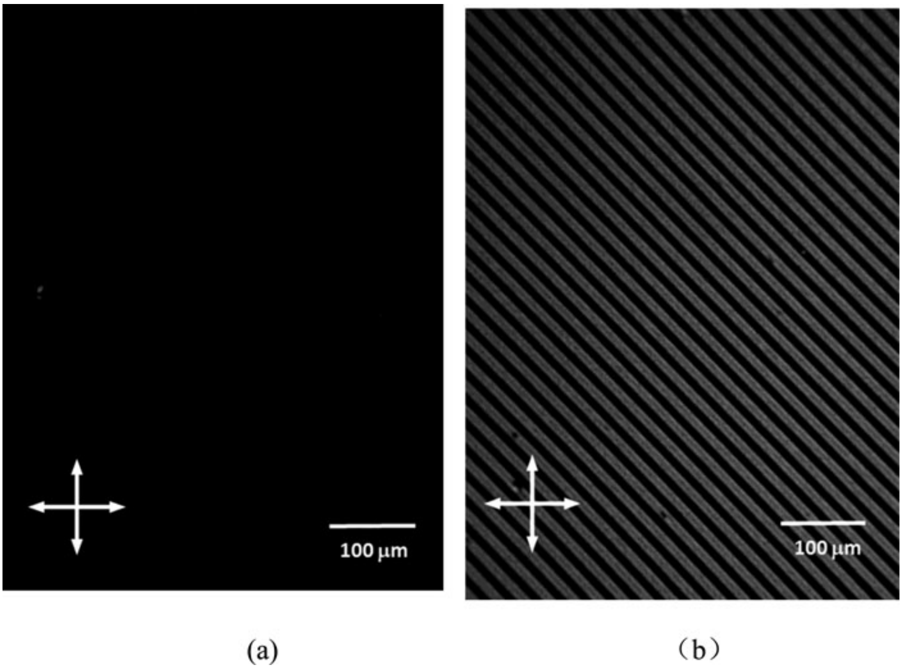

**Figure 5.** Photomicrographs shows optical textures of the discogen OPE10 confined in PDMS channels with the channels being aligned (a) parallel to and (b) to make 45° against the polariser, respectively. The channels were 10 $\mu$m wide and 8.2 $\mu$m deep. The white cross arrows in the pictures indicate the optical axes of the crossed polarisers of the microscope.

certain amount of substraction in the retardation when the two slow axes are perpendicular to each other (Fig 6b). For the discogen, the slow axis is perpendicular to the molecular axis, i.e. resides in the plane of the disc-like molecule. Therefore, we conclude that the discotic columns are aligned parallel to the channels.

It is seems that a DLC alignment can be easily achieved in the PDMS microchannels. However, a theoretical elucidation that can clearly explain the mechanism behind the molecular alignment has not yet found. An empirical description is given as follows. DLCs are anisotropic fluids in which molecules are spontaneously assembling into an ordered structure with their molecular axes orient parallel to the director $\mathbf{n}(\mathbf{r})$. In a standard angle expression, the director can be written as $\mathbf{n} = (\cos\theta \cos\phi, \cos\theta \sin\phi, \sin\theta)$, where $\theta$ is the tilt-angle measured from $z$-axis, and $\phi$ is the angle of orientation on the $xy$-plane measured anti-clockwise from the $x$-axis. When a DLC is confined in a long channel extended in $z$-direction, the interactions between the molecules and the bounding surfaces become a vital factor that determines the conformation of $\mathbf{n}$. As shown in a previous section, the molecules of OPE10 adopt the edge-on anchoring at the PDMS surface. If the edge-on anchoring of the molecules can be held at all surfaces of the channels with a small dimension (said in $\mu$m scale), the molecules can be strongly bounded to have their faces parallel to the xy-plane at any position along z-direction. In other words, the confinement will create a single easy direction, which orients along the axis of the channel, for the discogen, and thus a unique director $\mathbf{n}$ oriented parallel to z-direction (i.e. along the channels) is achieved. If the discotic molecules possess a perfect axial symmetry, a perfect edge-on anchoring could be achieved, and the molecular tilt will vanished, i.e. $\theta = 0$. In this case, the discogen can shake off all distortions, and form a perfect columnar phase with long-range orientation order in the confinement.

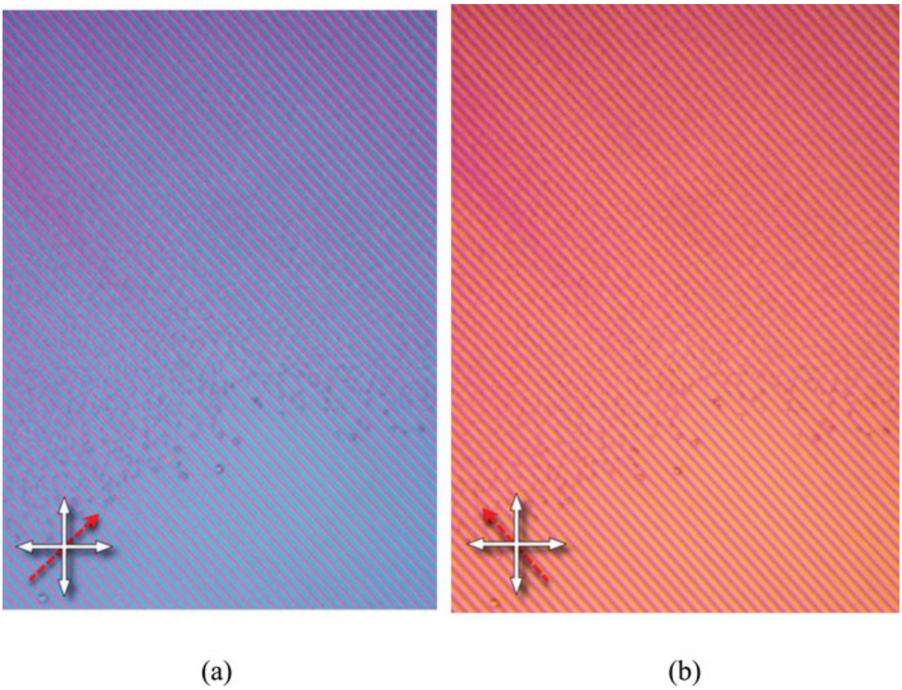
(a) (b)

**Figure 6.** Interference color patterns of the discogen OPE10 confined in PDMS microchannels when the slow axis of the phase compensator is aligned (a) perpendicular to the channels, and (b) parallel to the channels. The dashed red arrow denotes the direction of the slow axis of the phase compensator inserted into the optical path of the POM.

## 4. Conclusion

We have studied the molecular alignment of a discogen (OPE10) that is confined in a PDMS channel with a rectangular cross-section. A low energetic PDMS thin film is found to support the edge-on anchoring of the DLC. In the PDMS channels, the disc-like molecules adopt an edge-on anchoring at all surfaces of the channels, and the discogen is aligned with the discotic columns parallel to the channels. The simplicity of the geometrical structure of the rectangular channels may provide us an easy way to achieve desirable DLC alignment, and also a stepping stone for understanding a more complex system in a more complex manifold. The technical merits of the use of mould-replica based on PDMS include its easy process, low toxicity, and the topological structure of the channels can be precisely controllable.

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