

Printing of Monolithic Polymeric Microstructures Using Reactive Mesogens**

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While microcontact printing of thiol-based inks can lead to well-ordered self-assembled monolayers, the printing of polymeric materials (by any printing process) typically results in a poorly defined or randomized molecular structure. Here we demonstrate the printing of well-defined, defect-free polymeric microstructures with a soft lithographic technique based on liquid crystalline inks. Monolithic structures with tunable macromolecular organization can be locally printed with a variety of optical functionalities. This printing of reactive mesogens is shown to be potentially useful in the production of optical and/or electro-optical elements for LCDs and LEDs (e.g., color filters, retarders, and polarizers) and security-features.

Without doubt, replication techniques such as printing had a dominant influence on human civilization and history. A wide variety of printing techniques are commercially available including letterpress, offset printing, screen printing, inkjet printing, gravure printing, and flexography. Most of these printing processes are used in the reproduction of visual information and the choice for specific printing process is dictated by economy of scale, printing speed, print quality, and compatibility with full-color or glossy images.

In the last two or three decades, printing processes are also increasingly studied as an alternative for photolithography in the semiconductor industry. For instance, a whole family of techniques ("soft lithography") was developed for the nano- and microstructuring of inorganic matter.^[1-4] One of these techniques, called microcontact printing (μ CP), has received by far the most attention. In this technique, a soft elastomeric

stamp with a relief structure is used. This stamp easily establishes an intimate contact with a substrate in the raised areas of the stamp (conformal contact). In the most common case, the stamp is inked with an (alkane-)thiol which is transferred from the stamp to the gold substrate. The transferred ink forms a self assembled monolayer on the substrate and acts as an etch resist. Apart from organic molecules, the transfer of a wide range of materials such as proteins, colloids and polymers has been demonstrated.^[5-7] More recently, the use of inkjet printing has received a great deal of attention in, for instance, the manufacturing of polymeric light emitting diodes (PLEDs).^[8] Inkjet printing is used to deposit polymeric semiconductors in well-defined regions to produce monochrome or full-color devices. Again, a printing process is preferred above lithography for the microstructuring of a device or its components to facilitate large-scale production. Conventional printing processes usually result in polymeric structures with a poor or random orientation of the molecular chains. In the case of inkjet printing of polymers, for instance, the printed macromolecules exhibit a partial in-plane orientation or a random orientation dependent on the exact deposition conditions, i.e., an aligned, monolithic structure is usually not obtained.

A variety of polymeric thin films have been developed for flat panel displays, particularly for liquid crystal displays (LCDs) and light emitting diodes (LEDs). Usually, these films possess a well-defined, aligned, and monodomain structure. Typical examples of such layers are i) polarizers, retarders and color filters in LCDs; and ii) quarter wave films and polarizers in LEDs.^[9-11] Increasingly, these films are microstructured to enhance performance or to transfer the films inside the device ("in-cell optics").^[12,13] At the moment, these monolithic microstructures are predominantly produced via lithography and a need exists for high-speed printing processes to produce these microstructured polymers to increase production speed and to reduce costs. Apart from these display applications, other fields such as security technologies make use of patterned, monolithic optical layers. Genuine optical effects from polymer films are used to prevent fraud of valuable documents or products such as bank notes, tickets or consumer articles (e.g., watches, perfumes). Security features need frequent replacement because of counterfeit, and consequently there is continuous need of innovative security elements with new optical features.^[14,15]

Recently, Chiu and coworkers have employed a nanoimprinting lithographic technique to structure a thin layer of reactive liquid crystal (LC) photoresist.^[16] The resultant poly-

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meric film showed a well-defined grating topography on the surface. In addition the LC was aligned parallel to the grating lines using a modest imprinting pressure of 1.5 bar. This alignment is induced during the pressing stage owing to shear. The sub-micrometer pitch gratings obtained using this novel soft lithographic method are shown to be useful as retardation or alignment layers. Nanoimprinting usually results in accurate micro- and nanostructures starting from a continuous layer of prepolymer. This technique leaves a residual film of polymer over the area where the prepolymer has been applied and the achievement of isolated features on the target substrate requires additional etching steps that complicate the process. In addition, the patterning of different features with different functional inks is not straightforward using nanoimprinting. The search of new soft lithographic techniques for mesogens complementing the existing ones and overcoming their limitations is therefore needed.

In the present Communication we demonstrate a novel soft-lithographic technique for the printing of polymeric microstructures based on liquid crystalline inks with a defect-free and tunable macromolecular architecture. The method is based on a process which, to a large extent, resembles classical flexography. It relies on the transfer of a mesogenic ink from an inkpad to an organic or inorganic substrate with a polymeric alignment layer, using an elastomeric stamp. We demonstrate that by using this patterning technique, we can locally apply monolithic structures in the range of micrometers with different optical functionalities in one single step, in contrast to nanoimprinting which requires additional etching of the polymer layer. Sequential printing of different functional inks in one single substrate is straightforward using our methodology. Potential applications in the fields of displays and security devices are also shown.

Figure 1 shows schematically the employed method. An elastomeric stamp (polydimethylsiloxane, PDMS) with a raised image area is inked with a mesogenic compound. This is done by preparing a thin layer of the mesogenic material as an inkpad, and subsequently putting the stamp in contact with the inkpad with a controlled pressure. After some time the stamp is removed, and in this way the mesogen is transferred only to the raised areas of the stamp. After the inking step, the stamp is put in contact with the target substrate to perform the printing. This step, as well as the inking, can be performed at room temperature (RT) or at elevated temperature depending on the viscosity and/or phase behavior of the employed mesogen. After removal of the stamp a patterned layer of the mesogen with the image of the stamp remains on the substrate. An optimization with respect to printing pressure, time and temperature needs to be performed for each specific mesogen. The transferred image can comprise reactive and non-reactive liquid crystal (LC) molecules and other extra functionalities or additives. The target substrate can also be treated and/or structured to induce preferential orientation of the transferred mesogen, i.e., classical techniques such as rubbing/buffing and/or photo-alignment can be employed.^[17,18] In this way patterned LC structures in the micrometer range can

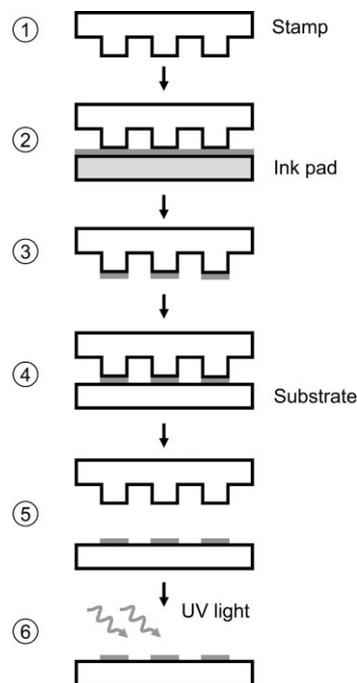


Figure 1. Schematic representation of the printing process. An elastomeric stamp (1) is inked by contacting it with an ink pad (2). The stamp is released from the ink pad (3) and then brought into contact with the target substrate (4). Afterwards the stamp is removed and an ink pattern is obtained on the substrate (5). Photocurable inks are usually polymerized using a UV flood exposure (6).

be obtained. In the case of reactive inks, polymerization can be performed either thermally or optically, generating mechanically stable and flexible polymeric structures.

We have proved this method by printing different mesogens on different substrates. Figure 2a shows a scanning electron microscopy (SEM) image of a PDMS stamp consisting on a square lattice (40 μm period) of truncated square pyramids with a top side length of 8 μm . Figure 2b shows a typical polarization microscopy image of a lattice of squares printed on glass using a non-reactive LC (E7). The squares are found over the whole contacted area (5 \times 5 mm^2) applying a rather low pressure of 0.4 bar. This material shows a nematic mesophase at RT and printing can be performed at this temperature. This figure illustrates that the microstructure of the stamp is accurately reproduced on the substrate. A close view of the printed squares shows a typical Schlieren texture from a nematic LC phase (inset Fig. 2b). We have also printed the same non-reactive mesogen on rubbed polyimide using the same procedure. Figure 2c shows a polarization microscope image of a pattern of squares printed on rubbed polyimide. The rubbing direction was parallel to one of the lattice vectors of the array and the picture is taken with this direction at 45° with respect to the transmission direction of the two crossed polarizers. Light transmission in the printed areas has its origin in the retardation introduced by the birefringent printed squares. This images shows that the transfer of mesogenic material from the stamp to the substrate is highly effective and

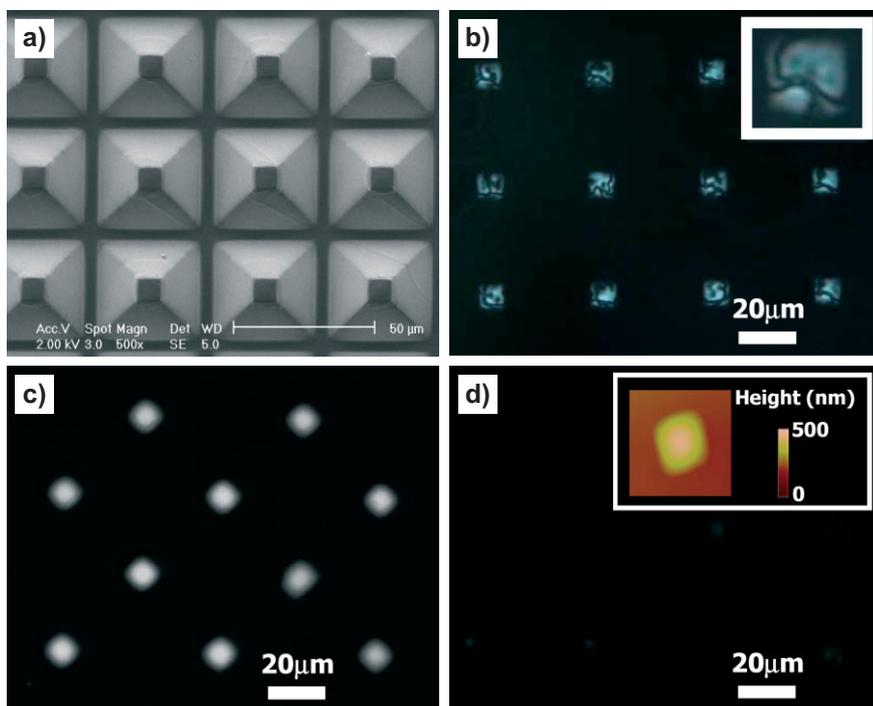


Figure 2. a) SEM image of the PDMS stamp. b) Polarization optical microscopy image of a pattern of squares printed on glass using a non-reactive LC. Inset shows a magnification of one of the printed squares. c,d) Polarization optical microscopy images of a pattern of squares printed on rubbed polyimide using a non-reactive LC (E7, Merck). The rubbing direction is parallel to one of the lattice vectors. The lattice vector is c) at 45° with respect to the transmission direction of the crossed polarizers, and d) parallel to the transmission direction of the crossed polarizer. The inset shows an AFM image of one of the printed squares using a reactive mesogen (RM 257).

reproducible and only minor differences can be found between neighbor squares. Total extinction is observed when the rubbing direction is parallel to the transmission direction of one of the crossed polarizers (Fig. 2d). These experiments illustrate that the molecular orientation of the LC is highly influenced by the boundary conditions of the target substrate. A multidomain structure with defects is obtained on non-aligning substrates such as glass (Fig. 2b) while a defect-free, monodomain structure is obtained if alignment layers such as

rubbed polyimide are employed (Fig. 2c and d). It is also possible to promote the planar alignment of the mesogens at the air boundary via the inclusion of planar surfactants for LCs. We have also investigated the patterning of reactive mesogens in order to obtain fully polymeric patterned structures. We have employed a reactive mesogen (RM257) with a nematic phase between 70 and 130 °C. The inking and printing steps were therefore performed at elevated temperature (80 °C) in the mesophase. After the curing step, an array of birefringent squares is patterned in the substrate. Features with sizes in the range of several micrometers were again obtained as in the case of the non reactive LC similar to Figure 2c and d. Inset of Figure 2d shows an AFM image of one of the printed squares having a height in the center of the square of around 250 nm that gives insight about the amount of deposited ink. Figure 3a shows a polarization microscope image of a patterned array of squares obtained printing reactive mesogens and using our printing method. The stamp employed in this case was an array of square-topped pyramids, where the inking-squares had a lateral dimension of 140 μm (within the range of the pixel size in LCDs). The rubbing direction was parallel to one of the lattice vectors of the array and the picture is taken with this direction at 45° with respect to the transmission direction of the two crossed polarizers. Color rings in the borders indicate differences in retardation that could be originated from differences in thickness which is confirmed by topographic measurements of the printed pixels (Fig. 3b) performed using an optical profilometer. This lack of thickness homogeneity prevents the use of these pixelated elements as retarders (quarter or half wave plates) since a more homogeneous optical property is required for this application. This is a drawback of our patterning method when compared with nanoimprinting in which the film thickness is better controlled.^[16] We can however envision other polymer pixelated layers making use of this planar configuration such as polarizers (by the simple inclusion of a dichroic dye) in which the inhomogeneity issue is not as critical.

It is also possible to pattern colour filters either based on absorptive processes, with the inclusion of dyes, or non-ab-

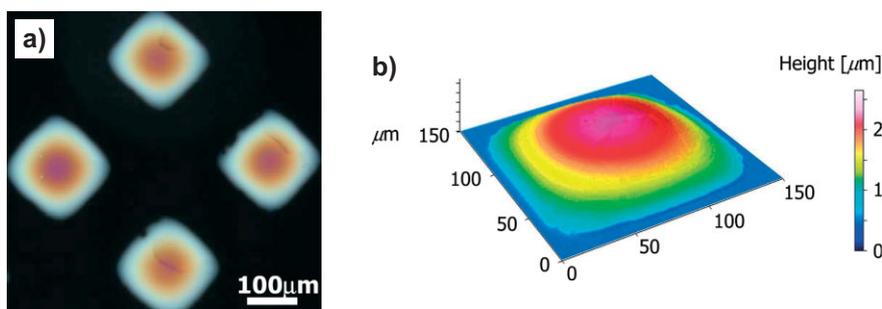


Figure 3. a) Polarization optical microscope images of a pattern of squares printed on rubbed polyimide using a reactive LC. The rubbing direction is parallel to one of the lattice vectors and it is at 45° with respect to the transmission direction of the crossed polarizers. b) Optical profilometer image of a single printed square.

sorptive processes, with the inclusion of chiral dopants (cholesteric filters).^[19] Cholesteric LCs have the ability to selectively reflect circularly polarized light of the proper handedness (with the same twisting sense as the cholesteric helix) and of a determined wavelength λ given by:

$$\lambda = \frac{n}{HTP \cdot x} \quad (1)$$

where n is the mean refractive index (i.e., the average of the ordinary and extraordinary index), x is the relative concentration in weight percent, and HTP is the helical twisting power of the chiral dopant. We have printed pixel size squares using three different inks comprising a reactive (non-chiral) monomer mixture and varying amounts of a cholesteric dopant which determines the reflected wavelength. Figure 4a–c shows three microscopy images (in reflective mode) of printed squares giving place to three different color reflections in the red, green, and blue (RGB) regions. In this case the changes in thickness of the printed squares have minor influence in the performance of the optical element (color filter). Figure 4d shows the transmission spectra of the red inkpad using left and right circularly polarized light. The spectra clearly indicate a strong polarization contrast between the transmitted and the reflected light within the reflection band. This kind of pixelated filters can, for instance, be used in reflective LCDs as disclosed by Lub et al.^[13] Full color displays can be generated using our patterning method by sequential printing of the three color filters in the same substrate.

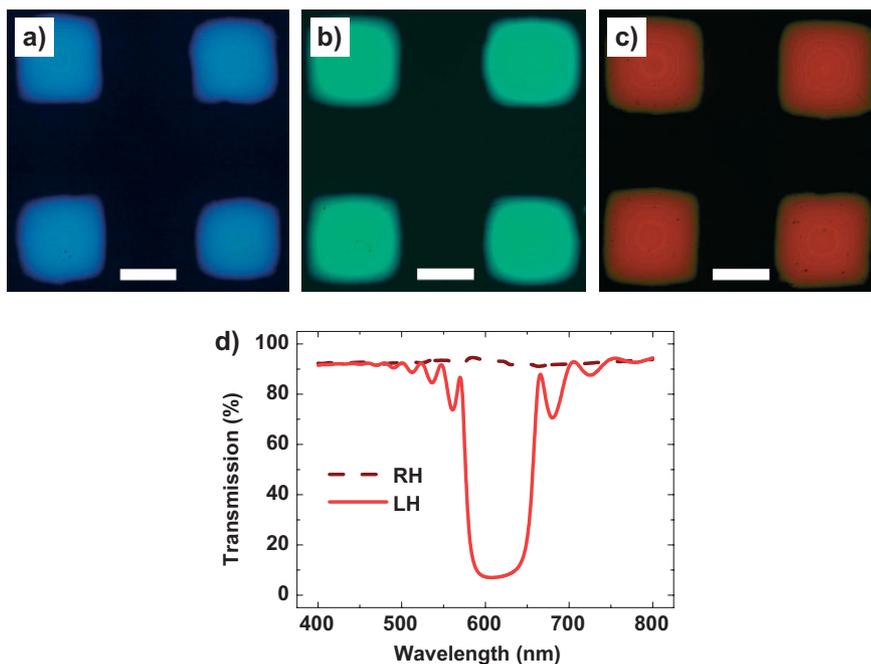


Figure 4. Reflective mode microscope image of a pattern of squares printed on rubbed polyimide using a reactive cholesteric LC giving a reflection band in the a) red, b) green, and c) blue. The scale bar is 100 μm . d) Transmission spectra of one of the inkpads for right and left handed circularly polarized light.

The Bragg properties and the polarization selectivity imposed by the helical molecular organization can also be used in the production of security elements. Figure 5 shows a print, obtained using a cholesteric liquid crystal ink, observed

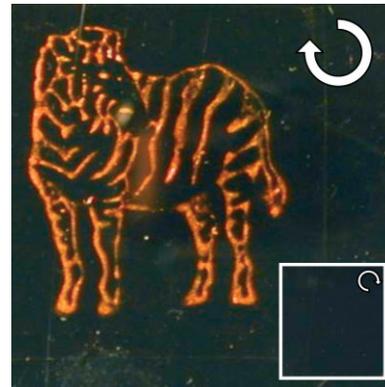


Figure 5. Printed element (approx. $2 \times 2 \text{ cm}^2$) using a reactive cholesteric LC visualized using a circular polarizer transmitting light with the same twisting sense as the cholesteric helix. Inset shows the same element but visualized using a circular polarizer transmitting light with opposite twisting sense as the cholesteric helix. A black sheet has been used as an absorbing background.

through a circular polarizer (consisting of a quarter waveplate and polarizer) of the same handedness than the cholesteric helix. Light transmitted by the polarizer is reflected making the print visible. In the inset of Figure 5 the circular polarized light and the helix have opposite handedness and no light is reflected. Apart from this polarization selectivity, the printed element also possesses the typical viewing angle dependence of cholesterics. By tilting from normal to glancing angles a shift to smaller wavelengths is observed with the naked eye. This kind of features cannot easily be reproduced and therefore can constitute the essence of a security-feature to be used in the certification of valuable documents or products.

In summary, we have shown a patterning method for the microstructuring of LCs using a soft lithographic technique. We have shown the possibility to locally print well defined squares of LC as small as 8 μm on a side. The use of reactive LC monomers can result in fully polymerized anisotropic patterns after curing. We have also shown the patterning of pixel-like squares with different optical functionalities: optical retarders using a planar configuration and a nematic LC, and color filters

using cholesteric LCs and a planar configuration. The production of security elements has also been demonstrated using this technique. Compared to the nanoimprinting of reactive mesogens the present technique allows the local printing of micrometer size features without the need of etching steps. In addition different types of functional elements can be easily applied to the same substrate by sequential printing employing different functional inks. A fine control of the molecular orientation is also done by combining the use of aligning surfaces, surfactants and the composition of the printed mesogen. Nanoimprinting allows on the other hand a better control of the topography. As in the case of soft lithographic techniques applied to the structuring of inorganic matter using SAMs, each of these techniques shows advantages and disadvantages making the choice of a specific one dependent on the requirements of the final structure being even some times the different techniques complementary.

Experimental

The commercial LC mixture E7 (Merck) was used as a non-reactive ink. A mixture of the reactive mesogen RM257 (Merck) with 1.0 wt % photo-initiator Irgacure 184 (Ciba) was used as reactive ink. The mixture to print cholesteric reactive liquid crystals contained RM257 and RM82 (Merck) in a ratio of 4 to 1, 1.0 wt % photo-initiator Irgacure 184, 1 % of planar surfactant (2-(*N*-ethylperfluorooctanesulfamido)ethylacryl from ABCR) and a left handed chiral dopant LC756 (BASF). The different percentages of chiral dopant to obtain different colors were 5.8 wt % (blue), 5.2 wt % (green), and 4.4 wt % (red). The PDMS stamps were made from Sylgard 184 (Dow Corning). Stamps were prepared by cast molding. This was done by mixing the base and curing agent in a 10:1 ratio, pouring the mixture onto the master with an square pattern complementary to that to be reproduced, and curing it for 24 h at 70 °C. The stamp was then released from the master at RT. The stamp (typically 5 × 5 mm²) was fixed to a glass plate through its unstructured side in order to allow easier handling. The inkpads were made by spin coating the mixture of liquid crystal dissolved in xylene onto a glass substrate. The spin coating conditions were maintained constant at 2000 rpm, 2000 rpm s⁻¹ for 45 s for each inepad. To obtain inkpads with a different thickness the ratio between reactive LC and xylene were changed. Target substrates were either glass or glass provided with an unidirectionally rubbed planar polyimide AL1051 (JSR).

The inking and printing of the substrates was performed using a home-built setup consisting of a weight-balance and a computer controlled spindle equipped with a vacuum chuck. The stamp was attached to the spindle by applying vacuum to the glass plate whereon the stamp was fixed. The substrate was placed on a hot plate that is positioned on the balance. The spindle is positioned perpendicular to the balance and the hot plate. The spindle was computer controlled and was moved downwards until a set force was applied (typically equivalent to a weight of 50 to 100 g during 30 s). This force was mea-

sured by the balance. After printing, the reactive ink was cured in an oxygen free atmosphere under a UV lamp to cross-link the monomers into a solid film at room temperature.

The polarization optical microscopy was performed with a Zeiss Light Microscope Axioplan 2. Transmission spectra were taken using a UV-3102 PC from Shimadzu. Left and right circularly polarized light was obtained by inserting a linear polarizer followed by a properly oriented quarter wave plate in the sample beam. Topographic images were obtained using an optical profilometer FOGALE Zoom Surf 3D (Fogale Nanotech) and an Atomic Force Microscope NanoScope Dimension 5000 with a Nanoscope III controller (Digital Instruments). SEM images of the stamp were taken using a PHILIPS XL30 ESEM-FEG.

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