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Formation of radial aligned and uniform nematic liquid crystal droplets via drop-on-demand inkjet printing into a partially-wet polymer layer

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This paper investigates the drop-on-demand inkjet printing of a nematic liquid crystal (LC) onto a variety of substrates. Achieving both a well-defined droplet boundary and uniformity of the LC director in printed droplets can be challenging when traditional alignment surfaces are employed. Despite the increasing popularity of inkjet printing LCs, the mechanisms that are involved during the deposition process such as drop impact, wetting and spreading have received very little attention, in the way of experiments, as viable routes for promoting alignment of the resultant LC droplets. In this work, radial alignment of the director and uniformity of the droplet boundary are achieved in combination via the use of a partially-wet polymer substrate, which makes use of the forces and flow generated during droplet impact and subsequent wetting process. Our findings could have important consequences for future LC inkjet applications, including the development of smart inks, printable sensors and lasers.

1. Introduction

Nematic liquid crystals (LCs) are a form of soft matter that, due to their anisotropic optical properties and sensitivity to an external electric field, have been fundamental in the development of flat-panel display technology [1]. A conventional LC device consists of a thin (< 10 µm) layer of LC sandwiched between two glass substrates that have been specially treated with an alignment layer, which ensures that the director (the average pointing direction of the molecules) aligns with a preferential orientation and/or tilt [2,3]. The deposition of the alignment layer typically involves a number of steps such as the baking of a thin (100 s nm) polyimide layer that is subsequently rubbed in order to promote a macroscopic and uniform alignment of the LC molecules parallel to the rubbing direction [3,4]. Other techniques that have been adopted to obtain a macroscopic and pre-defined alignment of the LC include the use of photoalignment layers, monolayers of surfactants, such as silane and lecithin, controlled evaporation of SiO films and flow induced alignment [5–8]. In all cases, achieving the desired alignment requires considerable preparation and treatment of the surfaces before the introduction of the LC material. To reduce the complexity in the fabrication process and to incorporate modern manufacturing techniques, such as inkjet printing, it would be highly desirable if the requirement of alignment layers and the corresponding processes could be relaxed.

In recent years, drop-on-demand (DoD) inkjet printing has proven to be a highly efficient and scalable fabrication process that allows for the accurate control of both the droplet size and volume, as well as the precise position where the fluid can be deposited onto the substrate. An additional benefit is that the technique allows for a variety of 'inks' to be printed simultaneously and at high speeds thereby increasing throughput. Furthermore, these inks can be deposited directly onto a range of substrate architectures including highly conformable substrates. Consequently, DoD inkjet printing is now employed to print a plethora of different materials, such as organic light emitting materials, particulate suspensions, conductive polymers and metalloids, for a range of industries and technologies including displays, pharmaceuticals, bioengineering and printed electronics [9–13]. Many of these applications have become more accessible to inkjet printing as it is now possible to print complex and non-Newtonian fluids such as liquid crystalline materials, which ordinarily possess surface tension and viscous properties that would otherwise make them incompatible with inkjet printing.

In the past six years, both bespoke and commercial inkjet printing systems have been used to deposit LC materials for a range of technological applications. For example, a report by Aliño et al. demonstrated the fabrication of monodisperse nematic LC dispersions by printing the

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LC onto a pretreated substrate before then rinsing the substrate with a Polyethylenimine solution thereby releasing the droplets into a dispersion [14]. The results presented therein clearly highlight the benefits of incorporating inkjet printing into the preparation process and the ability to prepare LC monodispersions for optical sensor applications. Additionally, Gardiner et al. have demonstrated that it is possible to print dye-doped chiral nematic LCs onto glass substrates to form optically-pumped thin film lasers [15]. Despite the rather non-uniform alignment (as evidenced from the optical polarizing microscope images), it was found that the helical axis was preferentially oriented normal to the glass substrates and consequently each droplet was found to act as a surface emitting micro-laser. In their report, it was shown that printing the chiral nematic LC directly onto a clean, but untreated glass substrate resulted in a uniform sessile droplet with diameters of ~300 μm. However, the alignment of the director within the droplet was found to be non-uniform and consisted of defects when viewed on a polarizing microscope. It was also noted that printing directly on to glass substrates that had been treated with rubbed and baked polyimide layers resulted in considerable wetting of the surface, which made them unsuitable for the purposes of printed laser sources. In order to achieve the standing helix configuration of the chiral nematic phase, the authors found that such an alignment could be obtained by printing onto a 50 μm-thick wet polymer layer that was coated onto the glass substrate prior to printing.

Given the findings reported in Ref. [15], the purpose of this study is to determine the conditions required to inkjet print a nematic LC onto a Poly(vinyl alcohol) (PVA) polymer layer so as to achieve a spherical and regular droplet perimeter along with a uniform LC director alignment. Both properties result from the precise conditions of the droplet impact and the subsequent interactions between the LC and the substrate surface. In accordance with the results reported in Ref. [15] for a chiral nematic LC, we find that the deposition of the nematic LC onto untreated glass substrates leads to sessile droplets, but with non-uniform alignment of the LC director. When printing a nematic LC on to rubbed polyimide glass substrates, however, droplets are found to consist of defects in the LC director alignment, although we do not observe significant wetting as noted in Ref. [15]. In this paper, we alter the drying conditions of the PVA layer to examine the formation of the droplet on dry, wet, and partially-wet polymer layers. It is found that the optimum droplet configuration of the nematic LC is obtained when the polymer layer is neither fully-wet nor fully-dry, but instead some condition in between whereby a uniform sessile droplet is formed with a uniform radial director alignment.

2. Experimental

2.1. Drop-on-demand printer and image capture

The experimental set-up that was used in this study was developed in-house and is shown in Fig. 1. The print-head used throughout the study was a MJ-ABP-01-80 dispenser (Microfab Technologies inc.) with an 80 μm nozzle diameter. The nematic LC chosen for this study was the nematogen mixture, E7 (Synthon Chemicals GmbH & Co.KG), which was supplied to the dispenser via a static pressure syringe pump. This nematic LC was chosen as its macroscopic physical properties, such as the refractive indices as well as the elastic and viscosity coefficients, are well-documented. Furthermore, it is liquid crystalline at room temperature and, importantly for printing, the isotropic phase (T_c = 58 °C) is readily accessible with the heating element fitted to our printhead. Two custom-made heating units with a 20 W heating element (DBK-HPOS, DBK Enclosures) and K-type thermocouple were used to control both the printhead and printing substrate temperatures to within 1 °C of accuracy.

Drop formation at the nozzle as well as the subsequent deposition onto the glass substrate was captured using a combination of a high-speed camera (Phantom V12.1) and a halogen high-intensity white light

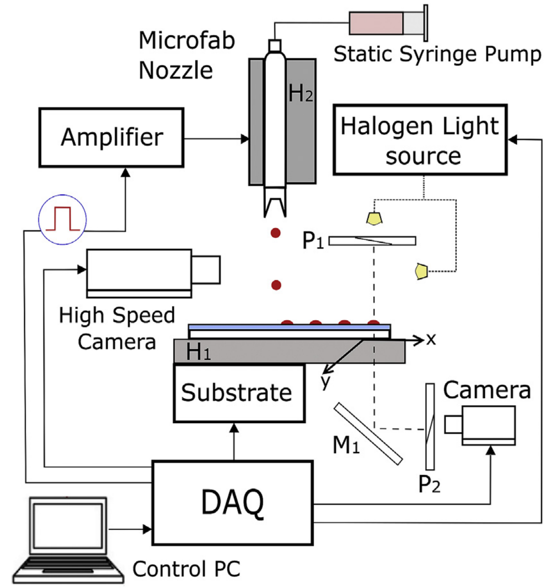

Fig. 1. A schematic showing the custom-built experimental apparatus used to print the nematic LC in this study. P_1 and P_2 are linear polarizers, H_1 and H_2 are the substrate and nozzle heating elements, respectively, and M_1 is a mirror.

source (OSL2 3200K, Thorlabs) that were arranged in a shadowgraphy configuration. The alignment of the director of the LC droplet shortly after deposition onto the substrate was analyzed using a CCD camera (DFK 23U274, The Imaging Source) with linear polarizers that were placed before and after the LC sample, with the transmission axes crossed (as shown in Fig. 1). Accurate positioning of the droplet was achieved using a custom-made x-y motorized stage that could be translated in 50 μm increments. Finally, timing synchronization, temperature control and printing specifications were achieved using a purpose-built LabVIEW program in combination with a computer-controlled DAQ card (NI USB-6351, National Instruments).

2.2. Printing conditions

The formation of repeatable and homogeneous droplets is critical in printing applications and, in the current study, was achieved by careful selection of the printing parameters. The default printing temperature was chosen to be above the clearing temperature, T_c of the LC, and unless stated otherwise the printing temperature was therefore maintained at 60 °C. At this temperature, the bulk viscosity of the LC is reduced from 75 mPa s to approximately 15 mPa s, which is sufficiently low to reliably deposit using inkjet printing. Additionally, at this temperature, the anisotropic components of the viscosity disappear, leading to increased homogeneity in the droplet properties. A 120 V square wave pulse was used to generate a single well-defined droplet (via push-mode, DoD) without the formation of satellite droplets, as can be seen in the inset of Fig. 2a. At this voltage, the resulting droplet velocity, which was determined from the analysis of the high-speed images, was found to be 1.6 ± 0.2 ms^{-1}.

Once the conditions for ejecting the nematic LC had been defined, the next stage was to consider the process of drop impact on the formation of the final printed droplet irrespective of the nature of the substrate. This process can be separated into two separate regimes: the mechanical impact and the subsequent wetting behavior. Initially, there is the transient process of impact between the LC droplet and the substrate, as seen in Fig. 2aii). The time-scale of droplet impact is given by $\frac{d}{u} = 50\mu s$, where d is the droplet diameter (before impact with the surface) and u is the droplet velocity. During this period a radial shear force and instantaneous fluid flow are generated in the LC droplet. It is worth noting that the duration of the impact process is an order of