Aligning lyotropic liquid crystals with unconventional organic layers

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Abstract—Lyotropic chromonic liquid crystals (LCLC) are a kind of LCs far less known and more difficult to control than conventional thermotropic nematics. Nevertheless, LCLCs are a preferred option – often the only one– for applications where hydrophilic materials must be employed. Being water-soluble, LCLC can be used in numerous biology related devices, for example in target detection in lab-on-chip devices. However, their properties and procedures to align them are still less explored, with only a very limited number of options available, especially for homeotropic alignment. In this work, novel organic alignment layers and alignment properties have been explored for selected LCLCs. Non-conventional organic alignment layers were tested and new suitable procedures and materials for both homogeneous and homeotropic alignments have been found.

Lyotropic chromonic liquid crystals (LCLC) are not as ubiquitous as their thermotropic nematic liquid crystal counterparts. However, their hydrophilic character make them perfect candidates for a number of specific applications, particularly those where biological materials are involved. In this context, LCLCs are being recognized as a simple and inexpensive method for detection of biologically active macromolecules or microorganisms [1-3] as well as a standard procedure for microparticle detection in hydrophilic media.

LCLCs are well suited for these applications, providing aligning surfaces compatible to aqueous media are employed. Organic alignment layers, such as polyimides and polyamides are well-known layers for conventional thermotropic liquid crystals. However, they are not commonly employed as alignment layers for lyotropic liquid crystals. LCLC can be aligned onto organic surfaces such as certain polymers, [4,5] graphene, parylene films, (PMMA) films, fluoropolymer films [6] or other techniques, such as micropatterned substrates [7]. The alignment of LCLC on inorganic surfaces such as SiO_2 and SiOx has been demonstrated elsewhere [8]

In this work, a study of novel alignment layers for water-based lyotropic liquid crystals has been carried out, testing new non-conventional layers, seldom utilized for thermotropic liquid crystal alignment. Some of the new tested compounds produced well aligned LCLC layers and two new layers were found to align the LCLC in homeotropic configuration.

Some of these layers are suitable to eventually work as a starting point for surface functionalization protocols in biological applications.

The lyotropic chromonic liquid crystals chosen were Sunset Yellow FCF (disodium 6-hydroxy-5-[(4-sulphonatophenyl)azo]naphthalene-2-sulphonate) and Cromolyn (sodium cromoglicate, a well-known traditional treatment for asthma), both being water-soluble salts of organic acids. Despite Cromolyn being more studied, Sunset Yellow (SSY) was preferred, because SSY presents a wider range of concentration where the nematic phase appears: 27% < N < 35% w/w at RT, (compared to Cromolyn: 13% < N < 17% w/w at RT) [9], as well as a wider temperature range where the nematic phase is present [10]. Besides, SSY viscosity is lower than that of Cromolyn in the working concentration ranges, making it more convenient to manipulate.

The following compounds were tested as alignment layers for SSY liquid crystal:

- Polymeric liquid crystal RMM34C (Merck)
- PDDA Poly(diallyldimethylammonium chloride) monolayer (Sigma-Aldrich)
- APTES ((3-Aminopropyl) triethoxysilane) (Sigma-Aldrich)
- NOA 60 and NOA 81 (Norland)

The alignment layers were deposited onto clean glass substrates using the following protocols:

- A polymeric liquid crystal RMM34C layer was obtained by filling up a standard cell with the precursor at 90ºC. Upon filling the cell, the layer was polymerized under UV light (365nm, 300s, 4mW/cm^2). After polymerization, the cell with an aligned freshly-obtained polymeric liquid crystal layer was disassembled and the substrates containing the polymer were assembled into new cells.
- PDDA monolayers were deposited by dip-coating: PDDA was diluted in deionized water at 0.2%. Substrates were first immersed in piranha solution,

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H_2SO_4:H_2O_2 (3:1) for 5 minutes. After washing in deionized water, they were dipped into the solution for 15 min and then dried with a nitrogen gun.

- APTES ((3-Aminopropyl) triethoxysilane) monolayers were prepared on SiO_2-coated glass substrates through a functionalization protocol as follows: first, the substrates were immersed in piranha solution for 5 minutes to induce the generation of OH groups. After washing in deionized water, the substrates were immersed in a 2% APTES solution in 95% EtOH for 10 minutes. The substrates were then washed in EtOH and baked at 110ºC for 1 hour.
- Norland Optical Adhesives, NOA60 and NOA81, were spin coated in glass substrates: 5s at 500rpm, and then 25s at 4500rpm with ramp. The layers were cured with UV exposure (365nm, 300s, 4mW/cm^2).

Cells were assembled and filled with Sunset Yellow in its nematic phase (33% w/w aqueous solutions). The cell thickness was 10µm. When possible, capillary filling was used, or else the cells were filled with positive pressure.

The alignment of liquid crystal layers was assessed by polarizing optical microscopy (POM), by comparing the transmission of cells parallel – to the filling direction and the rubbing direction if any– and rotated 45º with respect to the polarizers.

Figure 1 depicts the SSY alignment in cells with the alignment layer of a polymeric RMMA34C and PDDA monolayer (top and bottom respectively, for crossed polarizers at 0 and 45°). The viewing area is 25mm^2 approximately.

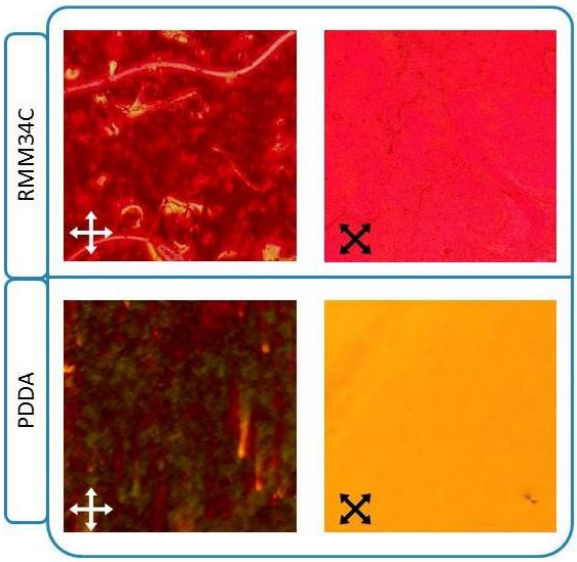

Fig.1. POM textures of liquid crystal Sunset Yellow in cells with an alignment layer of RMMA34C (top) and a PDDA monolayer (bottom), the arrows indicate the position of the crossed polarizers. Homogeneous alignment is obtained in both cases (PDDA is better aligned)

In both cases, the layers produced a homogeneous alignment of the SSY liquid crystal. In the case of polymeric layer RMM34C, the liquid crystal layer presented some misalignments scattered along the surface. Among other possible causes, these misalignments are mainly attributed to the poor wettability of LCLC on a polymeric surface. Indeed, the filling-up process of LCLC in the manufactured cells was hindered by the layers and produced numerous air bubbles inside the cells.

PDDA monolayers produced a homogeneous alignment as well. The layers presented minor defects as seen in Fig. 1, (bottom), but overall good alignment and contrast were obtained.

The cells prepared with APTES monolayers first produced, at the time of filling-up, a homogeneous alignment with good homogeneity and contrast with SSY, as shown in Fig. 2.

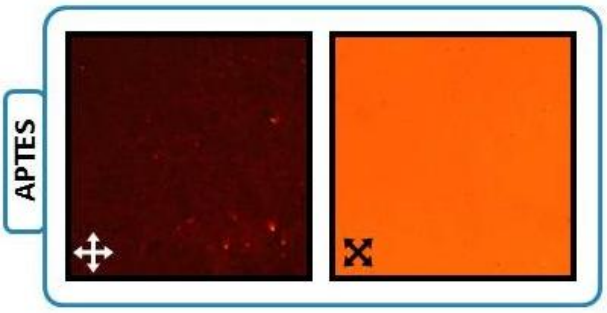

Fig. 2. POM textures for SSY liquid crystal with APTES as an alignment layer after finalizing the filling-up of the cell. A homogeneous alignment is produced, eventually evolving to homeotropic alignment.

However, this homogeneous alignment evolved into a striped transitory state that eventually became a perfect homeotropic alignment (Fig. 3). First, the SSY is aligned homogeneously in the direction of the flow when the cell is being filled up. At room temperature, a few minutes after the cell is completely filled up, the stripe patterns start to appear (2.5 minutes for a 10µm thick cell). The stripe patterns are aligned in the same direction as the LC homogeneous alignment. A few minutes later the patterns become more visible, start to tilt and dark areas of homeotropically aligned SSY show up. Figure 3d shows a detailed photo of the SSY alignment when changing from a homogenous to homeotropic alignment. Homeotropic and isotropic alignments are distinguished as the homeotropic cells become birefringent if slightly tilted. The stripped patterns are formed when the LCLC molecules start changing alignment and form twists with different handedness. Two neighbouring stripped patterns and the boundary wall formed between them can be seen as well.

The evolution from a homogeneous to perfect homeotropic alignment depends on the cell thickness and the liquid crystal flow upon filling up the cells. In the case of example in Fig. 3, the liquid crystal in the 10μm thick cell changed its alignment in a timeframe of 9.5 minutes.

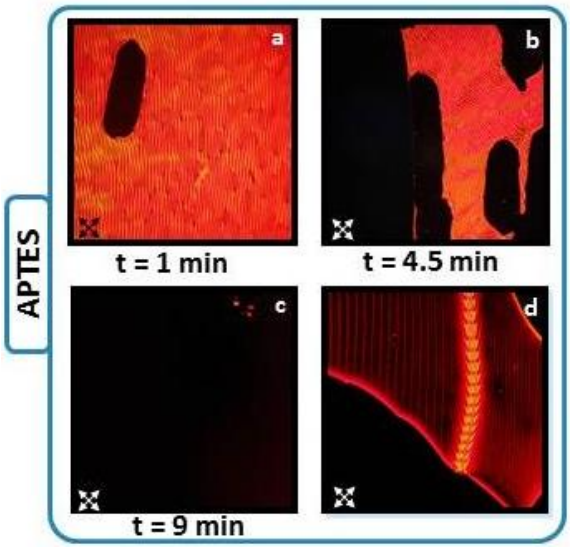

Fig.3. POM textures of SSY lyotropic liquid crystal in cells with an APTES monolayer, which produces a homogeneous alignment at first, which evolves into a perfectly aligned homeotropic layer (a,b,c). A stripped pattern detail can be observed when the SSY alignment is changing from homogeneous to homeotropic (d).

Norland optical adhesives (NOA) are usually employed besides their being used as adhesives. However, they can also be used with LCs to prepare a number of different polymer liquid crystals networks. For example, PDLC based photonic devices use mixtures of LC with NOA, as some of these adhesives are known to induce homeotropic orientation in standard nematic liquid crystals [11].

Glass cells containing NOA 60 or NOA 81 as alignment layers were prepared and tested with the SSY. NOA81 produced a remarkably good homeotropic alignment on SSY (Fig. 4, top), however, NOA 60 produced unaligned LC layers with numerous defects, (Fig. 4, bottom). The homeotropic alignment produced by NOA 81 was also evolved from a homogeneous alignment through the transitional stripped pattern as in an APTES monolayer.

The homeotropic alignment achieved in these surfaces can be related to non-covalent interactions between the LCLC molecules and alignment layers, such as hydrophobic interactions, π-π stacking or van der Waals interactions, as suggested in [6].

In conclusions, a number of non-conventional layers, rarely used for thermotropic LCs, have been prepared and tested for aligning lyotropic liquid crystals. Some of these layers resulted in very well aligned layers and are suitable candidates to produce both homogeneous and homeotropic alignment.

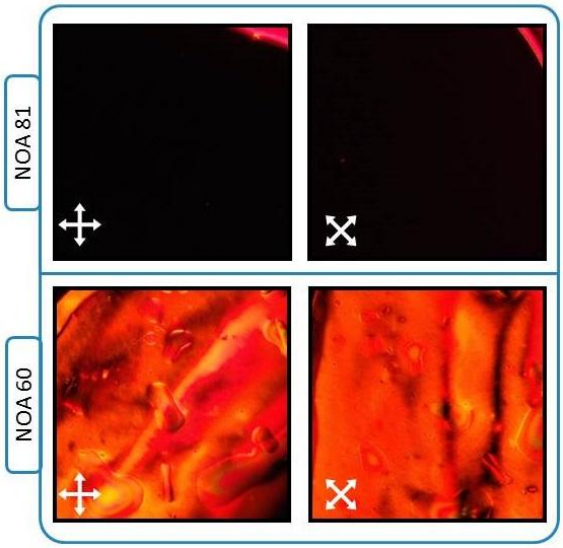

Fig.4. POM textures for SSY in NOA81 (top) and NOA60 (bottom) as alignment layers. In the top photographs, the edge of the cell, where the LC is not aligned, shows a good homeotropic alignment upon rotation of the stage.

A homeotropic alignment has been typically difficult to obtain and maintain over time for LCLCs. In this work we propose two new accessible and easy to obtain layers to achieve an excellent homeotropic alignment.

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