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Alignment of Chromonic Liquid Crystals: A Difficult Task

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We present our recent effort on chromonic liquid crystal alignment. In particular, we report the alignment behavior of chromonic molecules using different hydrophobic substrates.

Different materials have been used to this purpose but in all cases ribbons textures develop, indicating a slow water evaporation and/or a strong aggregation among molecules, that, as reported in a recent paper, give rise to threads connected through salt bridge bonds. Thin films of materials usually employed for thermotropic liquid crystals alignment induce schlieren textures that after 10 days evolve into ribbon textures; thin films of materials with a low surface energy orient molecules in homeotropic configuration, but the alignment is lost after two weeks as in the case of degenerate planar alignment.

Keywords Chromonic liquid crystals; alignment; surface energy

Introduction

The ability to control the organization of molecules in different aggregates is important for engineering desired properties such as photoconductivity, bio-sensitiveness, birefringence, DNA immobilization in gels for separation purposes [1,2].

Lyotropic Chromonic Liquid Crystals (LCLCs) are a class of molecules which, recently, have aroused interest among researchers; they are formed by water solutions of plank-like molecules with polyaromatic cores and peripheral groups. It is now recognized that chromonics embrace not only dyes and drugs, but also nucleic acids [3] and recently Bellini et al. reported the polymorphism of very short oligomers [4]. Biosensors are one important application of LCLCs. In general liquid crystal (LC) materials, with their birefringent properties and extreme sensitiveness to surface or surrounding environment, play an important role in these devices. Optical sensors using LC could eliminate the need of markers or tags, as these materials act to enhance the optical appearance of signals of a biological process.

It is advantageous that many biological systems, including cell membranes, phospholipids, cholesterols, DNA and so forth, exist in LC phases [5]. In literature a planar aligned chromonic LC can be distorted in presence of large particles by antigen-antibody interaction [6–9].

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LCLCs aggregate into columns which, in turn, show mesophase polymorphism, i.e. a nematic phase and a 2 dimensional phase (i.e. hexagonal) easily identified using a polarized optical microscope due to the high birefringence. A huge literature is reported in chromonic field, and in particular the most extensively studied chromonic mesogen is disodium chromoglycate (DSCG), an antiasthmatic drug marketed under the trade name "INTAL," examined initially in 1970s by Woodard and co-worker [10].

The molecules which constitute the chromonic systems are not amphiphilic, so these birefringent phases form a unique class of nonamphiphilic lyotropic liquid crystals [1]. Among chromonics, DSCG is studied also for its low temperature of nematic-isotropic transition. The model describing its molecular aggregation is still controversial, even if recently a new model for the assembly structure of molecular threads, which already exist in isotropic solution, [11] has been proposed. Salt bridges stacking on aromatic rings and hydration shell of DSCG cause a worm or polymer-like assembly that further interacts to form LC phases. The planar alignment of DSCG is well documented by the work of Lavrentovich and coworkers [12] and reviews on this subject are published by Lydon [13] and Collings [14].

Thermotropic nematic and smectic phases are usually aligned and used in LC devices and it is straightforward matter to produce planar, tilted or perpendicular alignment as required [13]. The alignment of chromonics aggregates, like DSCG, in cells, has proven to be difficult for several reasons. First of all, the birefringent phases are formed in water and in order to obtain long lasting devices it is necessary to almost suppress the water evaporation. After several attempts we have developed a method to prepare cells minimizing water evaporation as described in materials and methods. Secondly, several methods are reported in literature to obtain a good planar alignment [12], but the homeotropic alignment is not straightforward and it is important to carefully choose the materials. In literature one metastable homeotropic alignment [15] and one stable homeotropic anchoring are reported [16]. In this paper we report the behavior of DSCG using different hydrophobic materials as alignment layers, some of them employed for thermotropic LC.

Materials and Methods

Disodium chromoglycate (DSCG) (see Fig. 1), was purchased from Sigma Aldrich. All solutions of LCLCs were prepared with ultrapure water with a resistivity of 18.2 MΩ cm (Millipore, Synergy). Glass microscope slides (PEARL) were cut and cleaned in a NaOH bath, at 40°, sonicated and rinsed several times in distilled water.

As alignment layers we used Styrene-Butadiene-Styrene (SBS) 28% block copolymer (Sigma Aldrich) spin coated starting from a toluene solution and commercial mixed homeotropic and planar polymides (V PI and H PI) purchased from Japan Synthetic Rubber Co., dissolved and diluted in the standard solvent provided by the company, allowing the

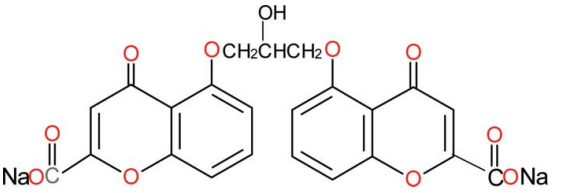

Figure 1. DSCG molecule.

components to mix. The former is an elastomer used in asphalt while the latter is used to control the surface pretilt angle of thermotropic LC [17]. In this case the solution was spin coated on glass surface, pre-annealed at 90°C for 5 min followed by hard baking at 230°C for 90 min where most imidization took place. A 5%wt solution of pure polybudatiene (PB), from Sigma Aldrich, in toluene was prepared and used after an equilibration time of 24 hours then spin coated and placed on a hot plate at 40° for 3 hours.

Aligning layers and chromonic solutions were prepared in a class 100 clean room, temperature controlled.

Cells were assembled using 12 microns mylar spacers and filled with DSCG (13% wt) in the isotropic phase (50°C) and then sealed by epoxy glue. At this concentration DSCG is nematic at room temperature. Some samples were prepared with a solution of DSCG (23% wt) in hexagonal phase. After allowing the glue to dry, the temperature was slowly decreased. This procedure allows to reduce the evaporation rate of the mixture contained in the cells.

To check the alignment of DSCG, observations by a Axioscope Zeiss polarized optical microscope (POM), equipped with a CCD color camera connected to a PC, were made at room temperature (25°C).

Results

The materials chosen for the alignment present a low surface energy: SBS is a copolymer which self-organizes into microdomains, lamellar, sphere or columns, depending on the concentration of the minority block (styrene, in this case). This material does not align thermotropic LC and it is dissolved by cianobiphenyls (data not shown). The cells prepared using SBS as alignment layer and DSCG in nematic phase are shown in Fig. 2a–b. No particular alignment is observed (Fig. 2a). After one week thread structures develop (Fig. 2b). Otherwise, the cells filled with solution in hexagonal phase (Fig. 2c and 2d) exhibit a peculiar texture.

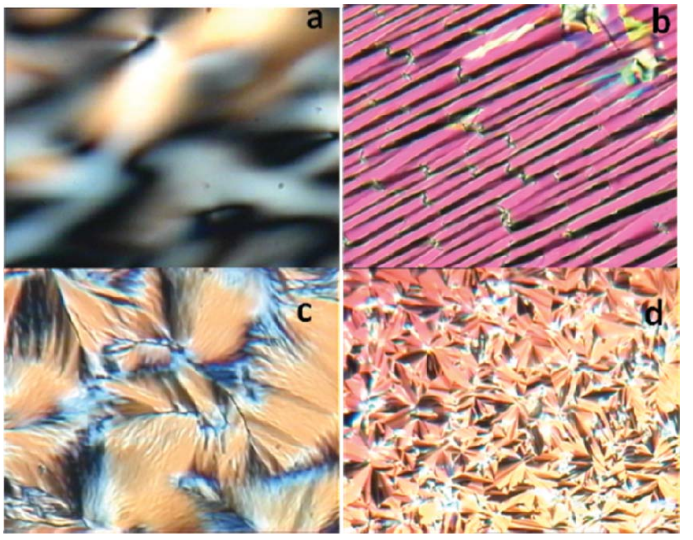

Figure 2. a), b) DSCG in nematic phase in SBS cell; c), d) DSCG in hexagonal phase in SBS cell.

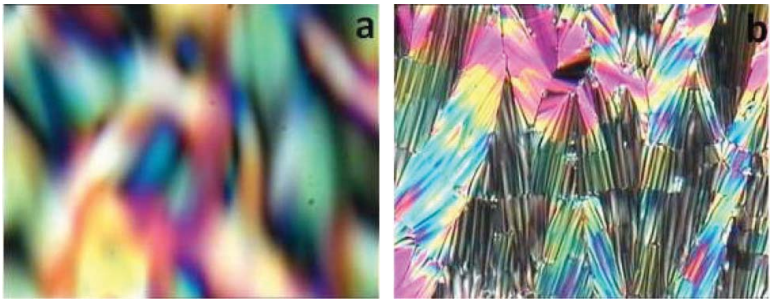

Figure 3. a) PI-5 cell just after filling, b) PI-5 cell after one week.

The structure is stable (Fig. 2c), but after weeks, a "crystallization" of the structure occurs, probably due to water evaporation, determined by a not perfect sealing of the cell. (Fig. 2d).

H PI and V PI mixtures, as reported in literature, allow to control thermotropic LC tilt angle varying the percentage of V PI in H PI; AFM analysis reveals the presence of nanostructures on the surfaces [18]. It has been demonstrated that strong hydrophobicity drives chromonic molecules perpendicularly to surfaces [16]. We chose H PI and V PI mixtures for their hydrophobicity and for the nanostructured surface in order to check if their presence could help in aligning homeotropically DSCG. We used three different percentages (5,10 and 15%), the samples are referred hereafter as PI-5, PI-10 and PI-15. The latter induces a degenerate planar alignment of the nematic phase, the so called schlieren texture appears and after some days evolves in herringbone texture (data not shown). However, for all cases, no easy axes are observed in the starting configuration nor in substrate plane neither perpendicular to the substrate. For PI-5 case (Fig. 3a), after one week the texture evolves in herringbone stripes.

The PI-10 cells are particularly interesting since they exhibit a more complex behavior when they are filled with DSCG in nematic or in hexagonal phase.

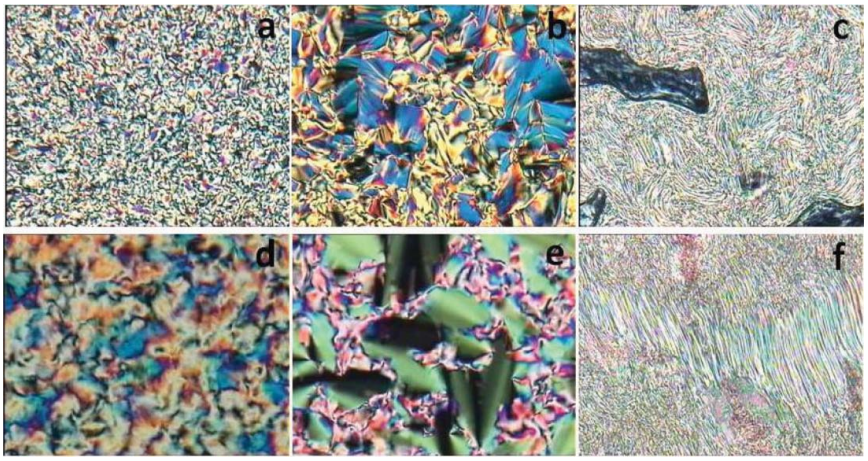

Figure 4. Time evolution of the cell: PI-10 a) nematic phase just after filling; b) nematic phase after 2 days; c) nematic phase after 8 days; d) hexagonal phase just after filling; e) hexagonal phase after 2 days; f) hexagonal phase after 8 days.

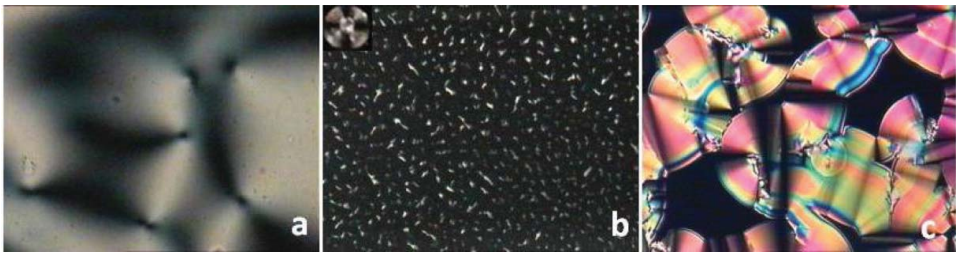

Figure 5. POM view of cell filled with DSCG in nematic phase. PB as alignment layer, a) just after filling; b) after 24 hrs, the characteristic cross of the homeotropic alignment in the conoscopic image is visible in the inset; and c) after 15 days.

In Figure 4 the optical images of cells made up using PI-10 and filled with DSCG in nematic phase (a,b,c) and in hexagonal phase (d,e,f) are shown. Even if for both phases, just after filling, the starting texture are different (Fig. 4 a,d), after 8 days the organization of the molecules seems very similar, i.e. "spaghetti-like" structure (Fig. 4 c,f). The cell filled with DSCG in hexagonal phase does not "crystallize" its structure like in SBS cell, but completely change the texture. Probably this is due to a different chemical environment at the surfaces that drives the molecules to organize in this way in order to minimize the energy.

Finally, we use polybutadiene, a rubber with low surface energy (33 mN/m) and the results are presented in Fig. 5. Cells made up using PB as alignment layer exhibit a peculiar behavior: after 24 hours the molecules, initially aligned in a degenerate planar configuration (Fig. 5a), change their orientation until perpendicular alignment of the easy axis respect to the substrate is reached. This final molecules orientation is stable in time, even if after 15 days the alignment is lost in favor of the so called "ribbon texture" (Fig. 5c).

Conclusions

In conclusion, we report on the behavior of LCLCs molecules when confined between hydrophobic surfaces. The cells studied here show a large variety of textures: degenerate planar alignment that evolves in herringbone textures, degenerate alignment that evolves in "spaghetti-like" configuration and homeotropic alignment in case of confining surfaces characterized by high hydrophobicity. Furthermore nematic and hexagonal phases behave in different way. We expected that nematic phase can be easily rearranged due to a lower viscosity with respect to hexagonal one. This is not completely true if the alignment layer is PI-15, since structure evolution occurs for both samples and after 8 days they reach the same final arrangement (spaghetti-like).

The experiments reported here suggest the following conclusion on the mechanisms that induce homeotropic alignment. It is clear that the confining surfaces play a key role but the strong hydrophobicity is not the only requirement to be fulfilled. In fact, for example, homeotropic polyimides mentioned in this work are optimized in order to align thermotropic LC so over hydrophobicity, chemical affinity is important. For example alkyl side chains can help in aligning homeotropically thermotropic LC [19] but their presence is not fundamental for chromonics. In fact, we tested silane derivatives (DMOAP) and one homeotropic PI from Nissan and we weren't able to obtain for DSCG an homeotropical anchoring. For this reason we used materials with low surface energy but without alkyl chains: SBS and PB. SBS surface energy is slightly higher than PB surface energy, but only

PB gives a satisfactory homeotropic alignment. Certainly numerical simulations, as the one reported in [20], could help in understanding the mechanisms involved in these systems and maybe suggest other surfaces more suitable as alignment layers.

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