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# Introductory Chapter: Liquid Crystals

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## 1. Introduction

The domain of liquid crystals represents an actual and dynamic scientific area, directly implied in top technologies as nanotechnologies, aerospace domain, microelectronics, and molecular biology [1]. For about 130 years, liquid crystals have been the subject of study for fundamental science and in many fields of research such as chemistry, physics, medicine, and engineering as well, which contributed to the progress in materials science and to innovative applications. In addition, as a result of the recent development of advanced synthetic methods and characterization techniques, the nanostructured liquid crystalline compounds that display special ordering properties and assign new functions have been highlighted, such as electro-optical effects, actuation, chromism, sensing, or templating [1–4].

Compared to other solid-state materials, liquid crystals present unique attributes, because they easily respond to external stimuli such as surfaces, light, heat, mechanical force, or electric and magnetic fields and eliminate defects by self-healing [5–9]. Thus, the understanding of the relationship between chemical structures of liquid crystalline compounds and their specific functions is becoming more important.

Liquid crystals are quintessential soft matter materials that present one to several distinct phases between the crystalline solid phase (Cr) and the isotropic liquid phase (Iso) [10–13]. These intermediary phases or mesophases not only possess some typical properties of a crystalline elastic solid like positional and orientational order as well as anisotropy of optical, electrical, and magnetic properties but also have the characteristic properties of an ordinary viscous liquid such as fluidity, formation and fusion of droplets, or mechanical properties [14–19]. Consequently, the compounds that present mesophases have intermediary symmetry properties, between an isotropic liquid and a crystalline solid; hence, a viscoelastic nature can be attributed to liquid crystals. Moreover, the unique combination of order and mobility represents the basis for self-assembly and supramolecular structure formation in technical systems. Generally, liquid crystals are elongated shape molecules, which are more or less parallel to each other in mesophases, contributing to anisotropic physical properties. These properties associated with their viscoelastic nature induce in liquid crystals the ability to easily respond under external stimuli and to change their configuration [20].

Depending on particular conditions where mesophases arise, liquid crystals have been classified into two classes: lyotropic and thermotropic. Thermotropic liquid crystals can be obtained either by heating a crystalline solid or by cooling an isotropic liquid. In the case of thermotropic liquid crystals, when the crystalline state is heated, the positional ordering of molecules vanishes but not the orientational one and so the

resultant ordered dynamic phase flows like a liquid and yet possesses the anisotropic properties of a crystal [21]. Upon further heating, this intermediary structure or mesophase loses as well the orientational ordering and transforms into a liquid. Unlike thermotropic liquid crystals, lyotropic liquid crystals are obtained by dissolving amphiphilic mesogen in a suitable solvent, to a specific concentration [22].

Most liquid crystals are organic molecules composed of  $\pi$ -conjugated systems and flexible alkyl chains attached to these. Although the functional conjugated units maintain the order, they have poor solubility in organic solvents, which limits the processing in optoelectronic devices [23]. Attachment of alkyl chains reduces the melting points and increases the solubility, while protecting the conjugated units from oxygen aggression. Hence, the optimum ratio between van der Waals interactions of the alkyl chains and  $\pi$ - $\pi$  interactions of the conjugated units results in modulation of physical states and optoelectronic properties of liquid crystals [24].

Based on different geometry of the constituents, liquid crystalline molecules have been classified into calamitic or rod-like (elongated molecules), discotic (disc-shaped molecules), and bent-core or banana-shaped molecules. Another classification was based on symmetry of phases, which changes during the phase transitions. Besides, the phase symmetry targets the molecular organization in the phases and determines the physical properties of liquid crystals.

While the small calamitic liquid crystal organic molecules have been used in LCD devices [25] and  $\pi$ -conjugated discotic liquid crystalline molecules proved to be adequate for electron transport [26] and photoluminescence [27], the supra-molecular unconventional liquid crystals based on non-covalent interactions and polymeric systems are used for high strength fibers, encapsulation of microelectronic circuits, actuators, and organic photovoltaic or renewable energy [28–30]. Additionally, the combination between nanoparticles (e.g. CNTs) and liquid crystals that promote the self-assembly into well-defined periodic structures represents another research domain that is dealing with the improvement of electro-optic characteristics in devices or obtaining metamaterials [31–36].

Between mesophases, the nematic phase (N) is the least ordered (since it exhibits only long-range orientational order) and more fluid (less viscous) and easily responds to electric fields or formation of a mono-domain liquid crystal phase, successfully applied to flat-panel displays [37]. When chiral mesogens are introduced into a liquid crystalline structure or chiral molecules are added to a liquid crystal phase, a chiral phase is generated. In a cholesteric mesophase or chiral nematic phase (N\*), the molecular orientation twists through the medium with a certain periodicity, while the positions of molecules are not correlated. Smectic phases (Sm) are distinguished from nematic ones by their stratification or ordering in the layers. Hence, in a smectic A mesophase, molecules may be on the average perpendicular to the layers; while in smectic C, the molecules adopt a uniformly tilted configuration, being inclined with a certain angle. The increase of molecular order leads to higher ordered smectic phases (Sm B, SmE, and SmG) [38]. The chiral smectic A phase (SmA\*) presents about the same structure as the achiral SmA phase, except the physical properties. On the other hand, the chiral smectic C phase (SmC\*) is different from any liquid crystalline phase and exhibits ferroelectric (FE) switching behavior.

Ferroelectricity appears in the case of molecules that present spontaneous and reversible electric polarization (P) that can be switched by using an external electric field [39, 40]. This physical phenomenon may be successfully accomplished by organic ferroelectric materials and used in devices like computer memories, sensors, and optics. In self-ordered liquid crystalline systems, ferroelectricity appears because of organization of chiral mesogens or the intrinsic dipole within achiral molecules,

which allows the facile switching of molecular dipoles. In mostly ordinary liquid crystalline phases (N, SmA, and SmC), the high rotational symmetry around the long molecular axis prevents the appearance of ferroelectricity. For chiral SmC\* phase, electro-optical effects with speeds below microsecond order have been registered, so that SmC\* liquid crystalline phase can be switched ON or OFF about  $10^3$  times more rapidly than nematic liquid crystals [41].

In liquid crystalline systems, chirality induces a one-dimensional helical structure, where the helical axis is perpendicular to the local director (for cholesteric mesophases) or is tilted from the normal layer so that the director precesses around the helix axis with a particular periodicity (for SmC\* phases) [42]. The remarkable behavior of SmC\* phases induced unique optical properties such as electro-optical effects, low-threshold laser emission, circular dichroism, or Bragg reflection [11, 43].

Similar to the SmC\* phase, the discotic phase containing pendant chiral side chains forms ferroelectric columnar phases, though the switching phenomenon is not very clear. However, two possibilities have been suggested: the entire column rotates  $180^\circ$  around the columnar axis or the molecules reorient independently [44].

Although bent-core (BC) molecules are non-chiral mesogens, polar properties were reported for this unconventional liquid crystalline class [45]. The novelty of BC structures arises from simple bending by approximately  $120^\circ$  of the mesogenic core, resulting in a compact packing arrangement of molecules, which restricts rotational freedom with high impact on the structure of the liquid crystalline phases. According to the polar axis direction in adjacent layers, these phases can show ferroelectric (FE) or antiferroelectric (AF) behavior. The switching process in BC compounds under an electric field influence has been associated with  $\pi$ - $\pi$  interaction type between the aromatic cycles that result after molecular restricted rotation around a tilted cone, while the chirality in the layers remains the same (the tilting and polar direction reverses) [46–55].

In order to be useful in devices, liquid crystals need to be forced and adequately aligned. Therefore, samples are formed between a pair of surface treated glass plates with about few microns distance. Compared to other mesophases, the alignment in the SmC\* phase is more difficult to obtain. By placing a ferroelectric liquid crystal sample between crossed polarizers with the director  $n$  aligned along one of the polarizers, the helix is suppressed by surface action. Hence, the sample becomes an electro-optic switch that shows spontaneous polarization and two surfaces which interact to stably unwind the spontaneous ferroelectric helix result. This is known as a surface-stabilized-ferroelectric-liquid-crystal (SSFLC) device, very attractive for display applications because of very fast switching response [56]. Thus, the SSFLCs are of great interest for electro-optic devices based on the memory effect. Moreover, another application of optically addressed SSFLC targets optical holography [57].

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