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Introductory Chapter: Nematic Liquid Crystals

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1. Nematic phase

The nematic (N) liquid crystalline phase is technologically the most important of the well-known and widely studied mesophases (nematic, smectic, cholesteric, and columnar). Nematics are also the most used, because they illustrate the best dual nature of liquid crystals. Hence, the molecules that form LC mesophases (intermediate states between the crystalline and liquid phase) display a unique combination of properties between long-range order and mobility, the basis of the numerous technical applications [1]. However, this combination constitutes as well an essential requirement for living matter, considering liquid crystals play a significant role in biomolecule's assembling, e.g., smectic phases (in phospholipid bilayer in the cell, protein filament), columnar phases (in DNA), or nematic phases (in chitin, collagen, cellulose, viruses, and silk) [2, 3].

Moreover, the ability of liquid crystal molecules to respond under weak external stimuli (temperature, electric or molecular adsorbates) stimulated the intellectual collaboration between specialists as chemists, physicists, or electrical engineers. As a result of joining of liquid crystal science and other fields, new opportunities for applications have been developed, involving polymers, colloids, or surfactants [4]. Hence, soft responsive materials based on surface-induced ordering transitions using nematic liquid crystal droplets dispersed within a medium or encapsulated into polymeric shells have been a promising perspective for experimental research [5].

The formation of liquid crystalline phase or mesomorphism implies the transition of a pure compound from an ordered crystalline state to a disordered liquid in two events: by a change in temperature and melting, the case of thermotropic liquid crystals, and by adding a suitable solvent to a mesogen and dissolving, the case of lyotropic liquid crystals. Thermotropic liquid crystalline state occurs mostly in compounds with pronounced molecular anisotropy. Lyotropic systems, representing two- or multi-component, occur when dissolved mesogenic amphiphiles self-assemble into ordered micelles.

Because of high mobility, nematic phases show a low viscosity, very similar to isotropic liquids, with the difference that the parallelism of the long axes induces the anisotropy of many physical properties. Hence, the nematic liquid crystals are anisotropic in respect to optical properties (double refraction), viscosity, magnetic and electric susceptibility, and electric and thermal conductivities [6].

The nematic phase is formed when the molecules are oriented to a common direction represented by a unit vector, n , or director. Hence, optical parallelism that depends on temperature is expressed quantitatively by order parameters S , which measures the degree of alignment of molecules' symmetry axes:

$$S = \frac{1}{2}(3\cos^2\theta - 1) \quad (1)$$

where θ is the angle between the director \mathbf{n} and the local molecular orientation, while $\langle \dots \rangle$ indicates the thermal average.

Subsequent discovery of a new type of nematic phase led to its classification into two subclasses: nematic uniaxial N_u (long-distance order in one preferred direction, when the director \mathbf{n} does not distinguish between head and tails) [7] and biaxial nematic N_b , characterized by three orthogonal directors (a primary director \mathbf{n} and two secondary directors \mathbf{l} and \mathbf{m}) [8]. Hence, the biaxial nematic phase has three different indices of refraction along the three spatial directions. In this case, the order parameter is better described by an asymmetric real tensor order parameter $\sim Q$ [9]:

$$\bar{Q} = \begin{bmatrix} \frac{S + \eta}{2} & 0 & 0 \\ 0 & -\frac{S - \eta}{2} & 0 \\ 0 & 0 & S \end{bmatrix} \quad (2)$$

In Eq. (2), η measures the degree of biaxial order along the secondary director, \mathbf{m} . When η is zero, it describes the uniaxial N_u phase, when S reduces to Eq. (1).

Confusions between molecular biaxiality and phase biaxiality are often created. In addition to the molecular aspect, the interactions between molecules, steric factors, dipoles, and the ordering anisotropy in the liquid crystalline structures are of decisive importance in observing the phase biaxiality. However, the higher the molecular biaxiality, the greater the chances of observing the phase biaxiality. Molecular modeling has played an important role in the study of the biaxial nematic; many papers, starting from mathematical considerations and based on potential models, deal with the simulation of molecular interactions and predict the observation of biaxiality in chosen systems. These models led to the identification of essential physical features, such as anisotropy, biaxiality, and electrostatic moments, and aimed at simulating bent-core systems [10] or disc/rod mixture systems or bent-core/rod mixture [11].

For a uniaxial nematic, the director can be aligned by a magnetic or electric field, so almost all liquid crystals display devices that used a uniaxial nematic phase. However, the biaxial nematic phase is technologically more important to exploit because of high sensitivity to magnetic or electric fields, flexoelectricity, or unusual rheological properties [8]. Hence, biaxial nematic liquid crystals can be successfully used for electro-optic switching or to control birefringence, considering negative dielectric anisotropy or lower viscosities associated with E-field reorientation of the transverse director about an aligned director \mathbf{n} . Potential applications of bent-core nematic liquid crystals target optical data storage, holographic media, photonics, or photoalignment of LC matrices [12, 13].

The alignment and switching of mesophases by an external field depend on polarization of liquid crystals and orientation of the dipole (parallel to the molecular axis or parallel to the column axis respectively). Liquid crystals that are responsive to electric fields show ferroelectric and antiferroelectric states. The main characteristic of ferroelectric liquid crystals (FLC) is the spontaneous polarization. Compared to uniaxial nematic phases that do not exhibit polar properties, considerable interest for technological applications represents the polar switching of biaxial nematic phases and fast response speed at low applied field strength, respectively (microseconds vs. milliseconds for achiral nematics) [14].

If the polar order in polar smectic phases arises from chirality or asymmetric close-packing constraints, in the case of biaxial nematics, ferroelectricity is the result of dipole–dipole interactions (the chiral polar phases are formed even in the case when the bent-core molecules are non-chiral).

The polar behavior of switchable phase was predicted by molecular dynamics simulations, which identify the structure–property relationships and evidenced the detailed perspective of the molecular organization in liquid crystalline phases. Hence, the nature of biaxial nematic consists of nanosized clusters of molecules or cybotactic groups [15].

2. Molecular shape of nematic mesogens

Materials that exhibit liquid crystalline phases are called mesogens. The relationship between the microscopic shape of mesogens that form the nematic phase and the macroscopic symmetry of the phase affect their physical properties. Hence, when designing a molecular structure, the aim is to influence and particularly enhance the molecular polarization.

The uniaxial nematic phase is found in simplest low molar mass liquid crystals or mesophases represented by compounds made up of long cylindrical-shaped molecules (calamitic mesogens) (**Figure 1a**) or discs (discotic mesogens) (**Figure 1b**); the biaxial nematic phase is found to be prevalent in bent-core compounds (banana mesogens) (**Figure 1c**).

The general structure of nematic liquid crystal compounds is composed of aromatic cycles which are planar, rigid, and polarizable, connected by conjugated double bonds along the long axis of the molecule. The rigidity of calamitic (rod-shaped) molecules provides the orientational order of the molecular axes, while their functionalization with one or two flexible hydrocarbon tails provides mobility by preventing these systems from crystallizing. Overall, an essential condition that must be met is the length of the molecule that should be greater than its diameter. The mesomorphism is generally enhanced by the presence of strong polar groups near the center of the molecule and by the weak polar groups at the extremities of the molecule.

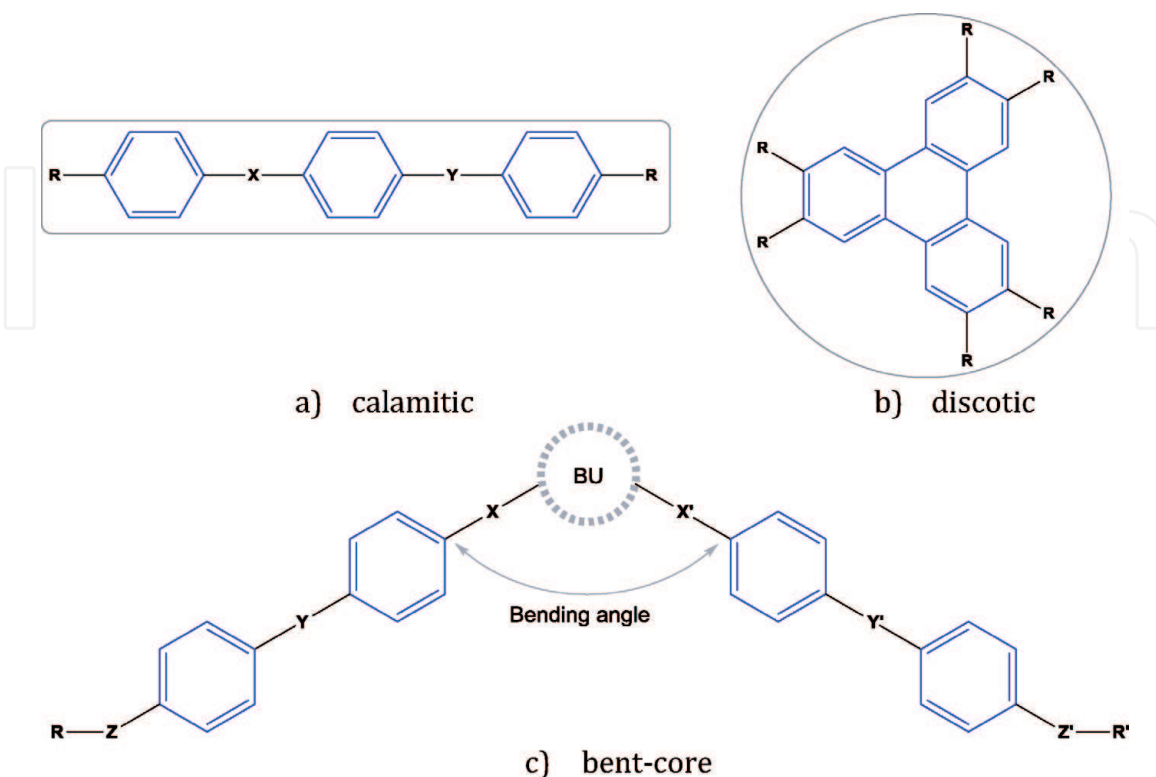


Figure 1.
 Typical structures in thermotropic nematic liquid crystals: (a) calamitic, (b) discotic, and (c) bent-core.

If molecular units from nematic mesogens are chiral molecules or mixtures of achiral molecules with optically active compounds, the molecular orientation of a nematic phase is distinguished by a helical modulation, a characteristic to the cholesteric phase, closely related to the nematic phase. They are of great technical importance for appliances with displays.

The length of bent-core molecules and the bending angle of the central unit are most important for the formation of polar ordered mesophases. Hence, a minimum number of rings between four and five are required (for three rings the system is stabilized by intramolecular H-bonding). Symmetric bent-core units (BU) comprising 2,7-disubstituted naphthalene derivatives show mesophases with highest thermal stability, while less symmetric biphenyl derivatives exhibit wide mesomorphic domains. Generally, increasing the size of the rigid bent unit increases the transition temperatures, so in order to obtain polar phases, longer terminal chains are required. The nature, position, and direction of the linking groups between the rings influence as well the ordering in mesophases; the most commonly used are ester and a combination of ester and imine groups. The obtaining of polar mesophases depends as well on the bending angle, which can vary between 105 and 140°.

In contrast to classical nematics formed by calamitic mesogens, nematic mesophases formed by bent-core mesogens exhibit unique properties, due to high packing density in a uniform direction and a polar order in the layers [15, 16]. As a result, they exhibit mesophases with a permanent polarization in the absence of an electric field (spontaneous symmetry breaking of achiral molecules and super helical structures).

For most rigid bent-core mesogens, nematic phases are rarely observed because of high tendency to associate into mesophases with positional long-range order. By contrast, flexible bent-core molecules form nanostructured nematic phases, including the twist-bend nematic phase discovered very recently [17]. Accordingly, the bent core nematic phase contains uniaxial, biaxial, and polar nematics and phases with tetrahedral symmetry [18].

3. Characterization of nematic mesophases

The most common techniques for characterization of nematic mesophases are polarized optical microscopy (POM), differential scanning calorimetry (DSC), X-ray scattering at wide and small angles (WAXS, SAXS), solid-state NMR, IR, and Raman spectroscopy [19].

Nematic phase is best highlighted in polarized optical microscopy, through which its fluidity and Schlieren texture are revealed (**Figure 2**). The method consists in observing the texture defects for which it was concluded that the presence of only the so-called two-brush disclinations is specific to the biaxial nematic mesophase and the presence of four-brush disclinations is characteristic of the uniaxial nematic mesophase. However, texture alone is not sufficient to determine whether the phase is uniaxial or biaxial. The microscopic method is considered less eloquent due to the influence of the sample preparation on the obtained image, surface effects, and the interaction between the liquid crystal sample molecules with the walls of the microscopic plate. It is used as an early method in identifying biaxial mesophase, but it must be accompanied by other methods in which no disruptive external factors are involved (e.g., solid-state NMR).

Conoscopy with and without a circular polarizer represents a valuable method to confirming biaxiality. This consists in looking at the interference image of a sample in the focal plane. The sample must be well aligned with the director n (homeotropic alignment) and oriented parallel to the incident light. The conoscopic

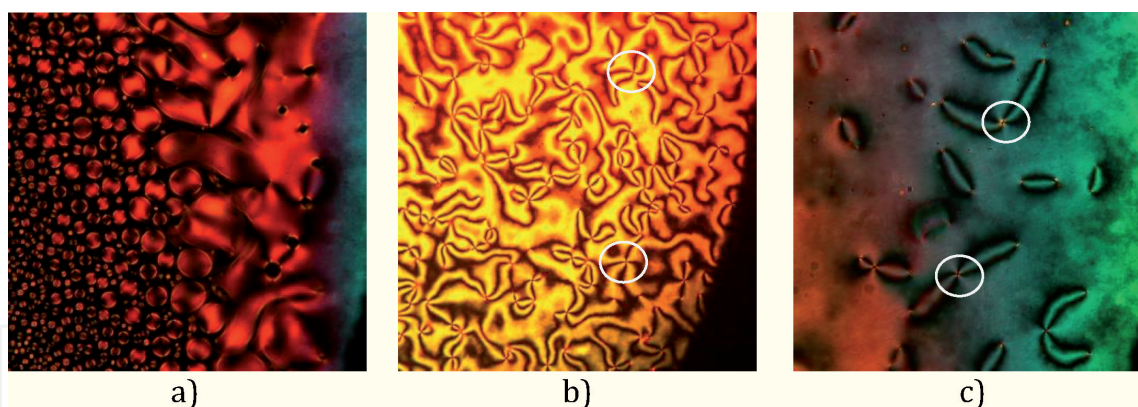


Figure 2.

(a) Nematic droplets, (b) Schlieren texture of a presumably uniaxial nematic (four-brush disclinations), and (c) Schlieren texture of a presumably biaxial nematic phase (two-brush disclinations).

image is characterized by the presence of so-called conoscopic isogyres that provide information about the axiality of the sample [8]. If the mesophase is uniaxial, the Maltese isogyre is observed, while if it is biaxial, a separation of the isogyres is observed, obtaining a characteristic conoscopic image.

Texture defects, singularities, or disclinations appear in the topology (arrangement of molecules) of a mesophase and are quantified by the factor S . The factor S is defined macroscopically, for the nematic mesophase, by the number of curves without birefringence (dark brushes) that meet in a point ($S = \text{no. of curves}/4$) and can have the values ± 1 (for uniaxial nematic) or $\pm 1/2$ (biaxial nematic) (**Figure 2**).

Differential scanning calorimetry signals, associated transition enthalpies and entropies, represent the first indications that a phase might be of special interest. Hence, the first-order nature of the transitions between crystalline, liquid crystalline, and disordered phase is evidenced. However, the second-order transitions of conventional uniaxial nematic phases N_u or polar biaxial N_b phases are difficult to detect only using the DSC technique, which gives only a clue of the existence of a mesophase; therefore a combination with other methods is required.

X-ray diffraction represents the most important method of identifying mesophases. The analysis of the position and intensity of X-ray reflections allows the complete description of the mesophase structure. For nematic phases, postulates is the proof of the presence of cybotactic clusters in the diffractogram of phases as related to biaxiality.

Additional analytical methods for characterizing mesophases include miscibility studies with known liquid crystals, electro-optical measurements, or light scattering to test for cluster formation in uniaxial nematics or ESR spectroscopy, dielectric spectroscopy, atomic force microscopy (AFM), and rheology.

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