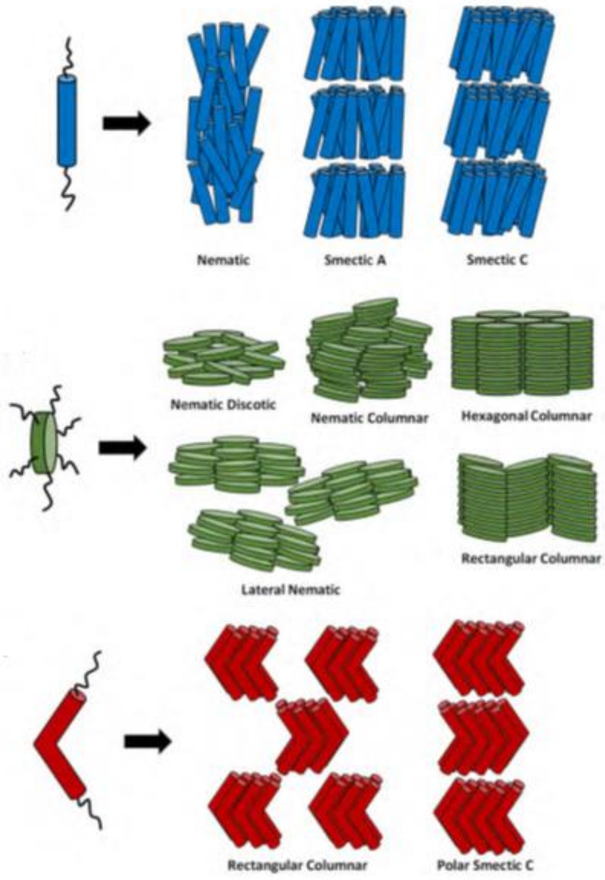
Chapter-1

Introduction

Abstract

This chapter explains the concept of liquid crystalline arrangement. Further, it also describes structure-property relationships in discotic materials followed by characterizing techniques that aid the information about the liquid crystalline arrangement.



1.1 Introduction:

Self-assembly is a process where the spontaneous arrangement of objects to ordered structures takes place under the influence of non-covalent interactions[1]. The self-assembly process occurs in materials at all scales ranging from subatomic particles to macromolecular substances (**Figure 1**). The morphology of self-assembled structures is always a function of shape, mode of interactions and homogeneity of the precursors. The interactions present in these structures is based on the nature of precursors in terms of their shape, charge, polarizability, dipole moment, mass, etc;

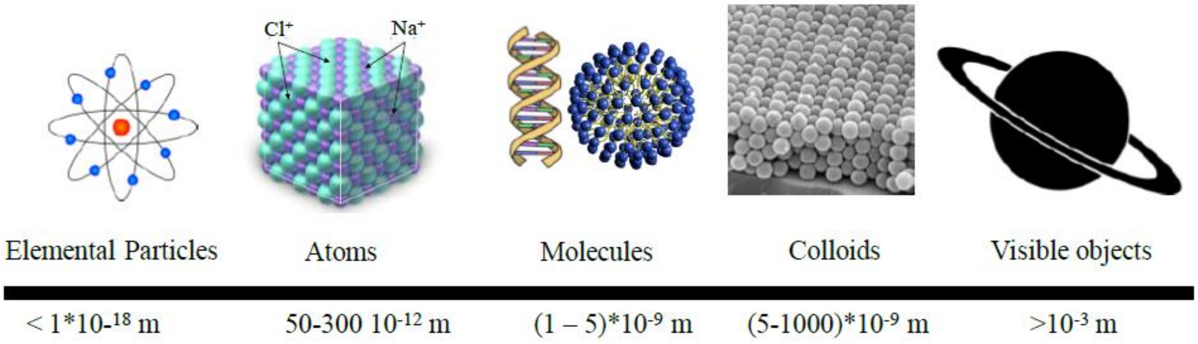


Figure 1: Self-assembly at all scales[1].

The building blocks of self assembly which have chemical functionality (have scope of reactivity and directionality) can restrict and tune the assembly process towards formation of thermodynamically stable structures. The intermolecular forces can be fine-tuned by modifying the molecular architecture. For instance, the presence of hydrogens atoms in a molecule covalently bound to an electronegative atom (such as oxygen or halides) can be used to increase the molecular interactions (H-bonding) and produce stable assembled structures. Molecular self-assembly has been found to be a spontaneous process since it is driven by the minimization of Gibbs free energy. The formation of ordered structures due to self-assembly implies that there is a reduction in entropy ($\Delta S > 0$). The spontaneity of the molecular assembly process is determined solely by the enthalpic factor. The enthalpy of the molecular self-assembly process is generally a function of intermolecular interactions (either molecule-molecule or solvent-molecule). Liquid crystalline systems are one of the widely known molecularly self assembles structures. This thesis involves the study of liquid crystalline systems. The rest of the chapter deals with information about liquid crystalline systems and their importance.

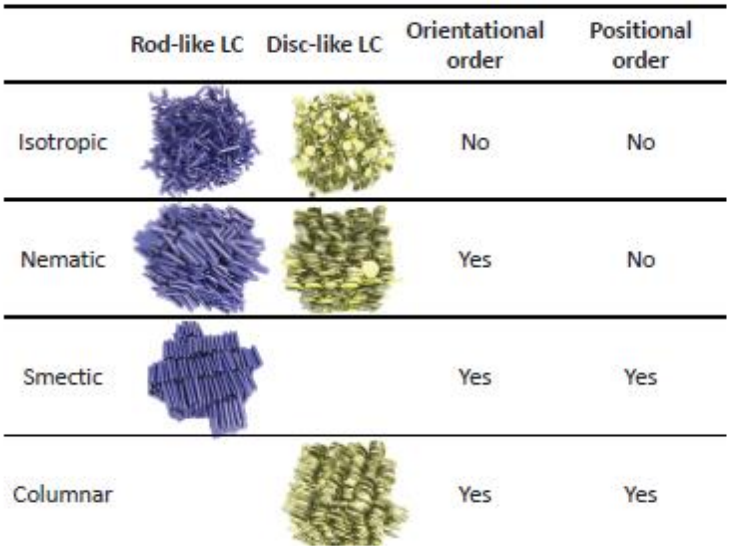
1.2 Liquid crystals

Liquid crystals are one of the prominent categories of soft matter which are known for their order and mobility. They have been thought of as the fourth state of matter in addition to solids, liquids, and gases. The important parameters which distinguish different phases of condensed matter are

- ***Positional order***: Positional order refers to the extent to which the positions of center of mass of molecules or groups of molecules, on average, show translational symmetry.
- ***Orientational order***: Orientational order refers to the extent to which the molecules align along a specific direction on a long-range basis.

In a crystalline solid, molecules are ordered in both the above ways, i.e. they are constrained to occupy specific sites in a lattice and to point their molecular axes in specific directions. On the other hand, molecules in a liquid diffuse randomly throughout the sample without any orientational order. Thus, a crystal has an orientational and three-dimensional positional order, whereas a liquid has none. Many crystals show phase transition corresponding to retention of position order and loss of orientational order which is termed as plastic crystals. On the other hand, Liquid crystal (LC) phases have been associated with long-range orientational order, with varying degrees of positional order. Liquid crystals are also called as mesophases because they are thermodynamically stable state of matter which is intermediate to that of both ordered solids and mobile liquids. The ability of the molecules to move among the various lattice sites induces fluidity to these structures, but since all directions within the phase are not identical, they are anisotropic rather than isotropic fluids. So liquid crystals combine the anisotropic properties of solids and fluidity of liquids. Since these anisotropic ordered fluids lie in between solids and liquids and possess properties of both, they are called intermediate phases or *mesophases*. Compounds which show mesophases are called as mesogens. The molecules in liquid crystalline state are free to move as in isotropic phase, but they remain oriented themselves in a certain direction. The extent of the orientation order of molecules in the mesophase is not like that of crystals. A compound can exhibit multiple mesophases depending on the degree of positional and orientational order of mesogenic molecules

(**Figure 2**). Liquid crystals are different from amorphous substances as follows, in the amorphous phase, the molecules are fixed in place, but they are arranged more or less randomly, and unlike in the liquid and liquid crystal state, they do not diffuse throughout the substance. Typical crystal to liquid crystal to isotropic transition is given in figure3.



	Rod-like LC	Disc-like LC	Orientational order	Positional order
Isotropic			No	No
Nematic			Yes	No
Smectic			Yes	Yes
Columnar			Yes	Yes

Figure 2: comparison of different liquid crystals based on order[2]

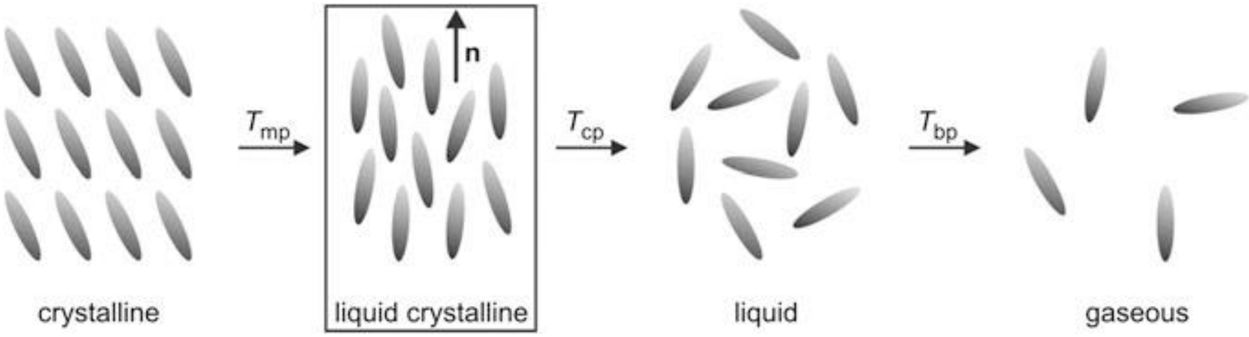


Figure 3: Liquid crystals vs Other states of matter

Liquid crystalline materials can be considered as anisotropic liquids as they appear soft and fluid, but at the same time possess anisotropic physical properties i.e refractive index, dielectric permittivity, magnetic susceptibility, mechanical properties, *etc*. depending on the direction in which they are measured. The fascinating combination of order and mobility allows these soft materials to respond to external stimuli, such as mechanical forces and electric or magnetic fields. (**Figure 3, Figure 4 &Figure 5**)

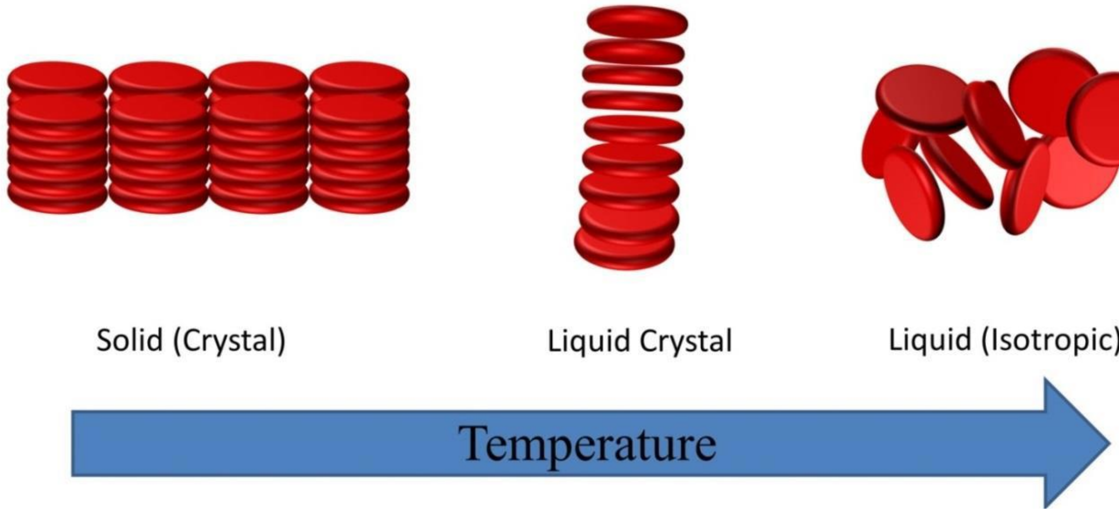
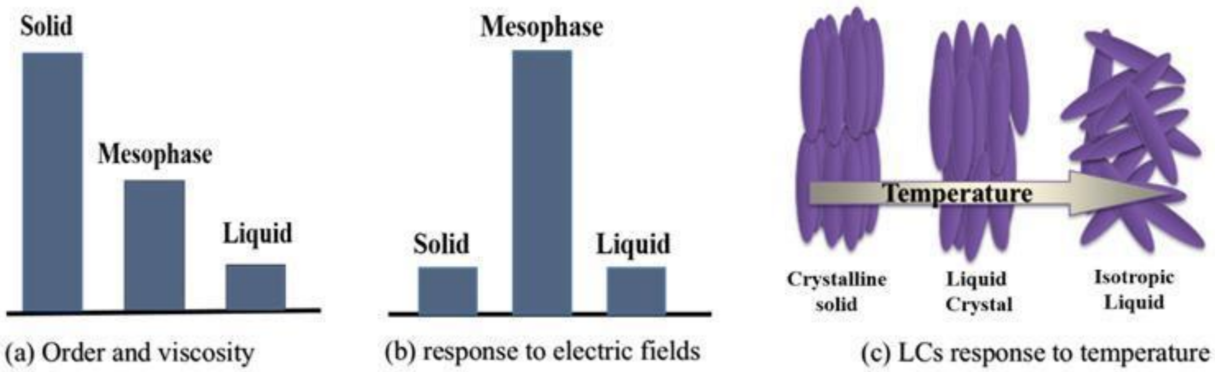


Figure 4: Typical behavior of thermotropic systems

The main factors driving mesophase behavior in a system are as follows [3]

- Anisometric interactions (differential expansion of molecules along three-axis)
- Attractive interactions (aggregation due to non-covalent interaction
- Repulsive interactions (phase segregation among incompatible parts in the molecule



(a) Order and viscosity (b) response to electric fields (c) LCs response to temperature

Figure 5: Comparison of Physical Properties of Liquid crystals with other states of matter

1.3 History of liquid crystals:[4]

During the period of 1850-1888, there were many reports on the unusual behavior of materials when they are heated towards their melting point. W.Heintz a German biochemist has reported the synthesis of a triglyceride by name stearin which exhibited cloudy liquid on heating before turning to clear liquid (**Figure 6**).

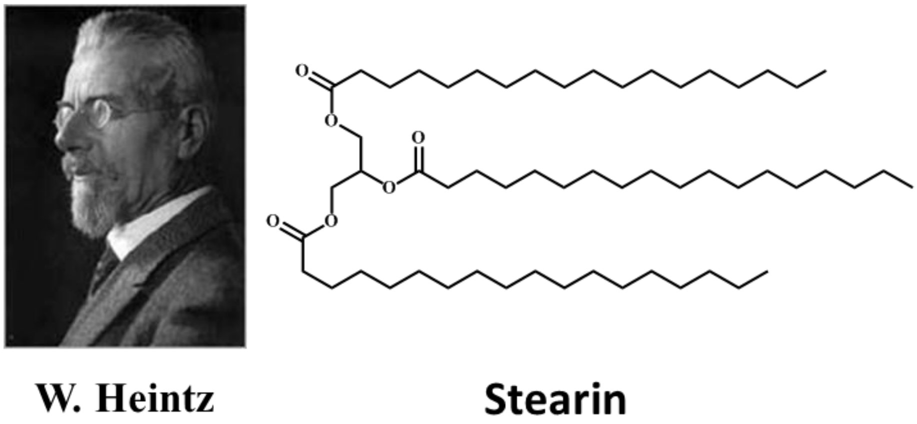


Figure 6: Photograph of W. Heintz, and structure of stearin molecule

In 1888, Reinitzer who was studying cholesteryl esters (**Figure 7**) observed that the isolated cholesteryl benzoates from carrot extracts showed double melting behavior as seen in stearins. Further, the phase changes were associated with birefringence and iridescent color changes.

Further, the cholesteryl benzoates were found to have optical properties as that of solid with flowing tendency as liquids. Reinitzers results were further confirmed by Viennese chemist von Zephraovich stating the crystalline nature of intermediate fluids.

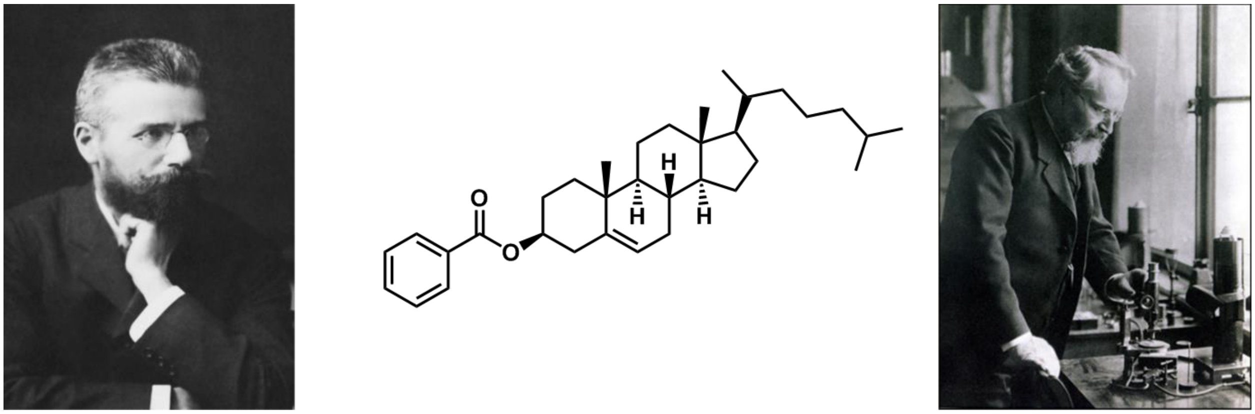
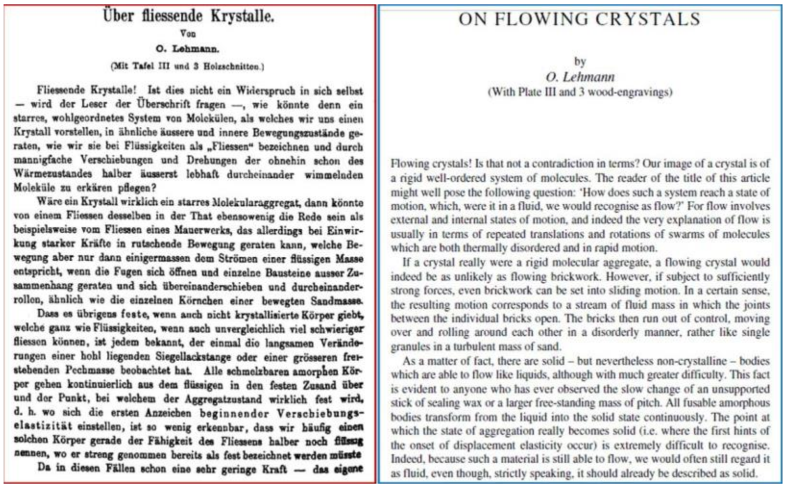


Figure 7: Reinitzer (left), Otto Lehmann (right), cholesteryl Benzoate(center)

Reinitzer sought help from German physicist otto Lehmann (1855-1922), Aachen University by reporting this reversible transitions of cholesteryl esters. Lehmann who is known for the first use of hot stage polarizing microscope for materials research analyzed these materials through hot stage polarizing microscope and termed them as, 'flüssige Krystalle' or, 'flowing crystals.' (**Figure 8**) (Liquid crystals). Today, the hot stage and polarized optical microscopes are one of the vital requirements for liquid crystal research. The first publication on liquid crystals was done by Reinitzer on the strange melting behavior of cholesteryl esters ('Beiträge zur Kenntnis des Cholesterins' (i.e. "Contributions to the Knowledge of Cholesterols") [5,6].

Lehmann continued his research on these liquid crystals and made very important observations using his combination of a hot stage-and-polarized optical microscope. He established the control of the microscope to study various phase transitions involved in these substances. Lehmann's paper, 'Über fliessende Krystalle' (i.e. 'On Flowing Crystals'), presented on October 25, 1889, showing the scientific community a new arena of materials research which laid the foundation of the science of liquid crystals [7].



Über fliessende Krystalle.

Von

O. Lehmann.

(Mit Tafel III und 3 Holzschnitten.)

Fliessende Krystalle! Ist dies nicht ein Widerspruch in sich selbst — wird der Leser der Überschrift fragen —, wie könnte denn ein starres, wohlgeordnetes System von Molekülen, als welches wir uns einen Krystall vorstellen, in ähnliche äussere und innere Bewegungszustände geraten, wie wir sie bei Flüssigkeiten als „Fliessen" bezeichnen und durch mannigfache Verschiebungen und Drehungen der ohnehin schon des Wärmezustandes halber äusserst lebhaft durcheinander wimmelnden Moleküle zu erkären pflegen?

Wäre ein Krystall wirklich ein starres Molekularaggregat, dann könnte von einem Fliessen desselben in der That ebensowenig die Rede sein als beispielsweise vom Fliessen eines Mauerwerks, das allerdings bei Einwirkung starker Kräfte in rutschende Bewegung geraten kann, welche Bewegung aber nur dann einigermassen dem Strömen einer flüssigen Masse entspricht, wenn die Fugen sich öffnen und einzelne Bausteine ausser Zusammenhang geraten und sich übereinanderschieben und durcheinanderrollen, ähnlich wie die einzelnen Körnchen einer bewegten Sandmasse.

Dass es übrigens feste, wenn auch nicht krystallisierte Körper giebt, welche ganz wie Flüssigkeiten, wenn auch unvergleichlich viel schwieriger fliessen können, ist jedem bekannt, der einmal die langsamen Veränderungen einer hohl liegenden Siegellackstange oder einer grösseren freistehenden Pechmasse beobachtet hat. Alle schmelzbaren amorphen Körper gehen kontinuierlich aus dem flüssigen in den festen Zusand über und der Punkt, bei welchem der Aggregatzustand wirklich fest wird, d. h. wo sich die ersten Anzeichen beginnender Verschiebungselastizität einstellen, ist so wenig erkennbar, dass wir häufig einen solchen Körper gerade der Fähigkeit des Fliessens halber noch flüssig nennen, wo er streng genommen bereits als fest bezeichnet werden müsste

Da in diesen Fällen schon eine sehr geringe Kraft — das eigene

ON FLOWING CRYSTALS

by

O. Lehmann

(With Plate III and 3 wood-engravings)

Flowing crystals! Is that not a contradiction in terms? Our image of a crystal is of a rigid well-ordered system of molecules. The reader of the title of this article might well pose the following question: 'How does such a system reach a state of motion, which, were it in a fluid, we would recognise as flow?' For flow involves external and internal states of motion, and indeed the very explanation of flow is usually in terms of repeated translations and rotations of swarms of molecules which are both thermally disordered and in rapid motion.

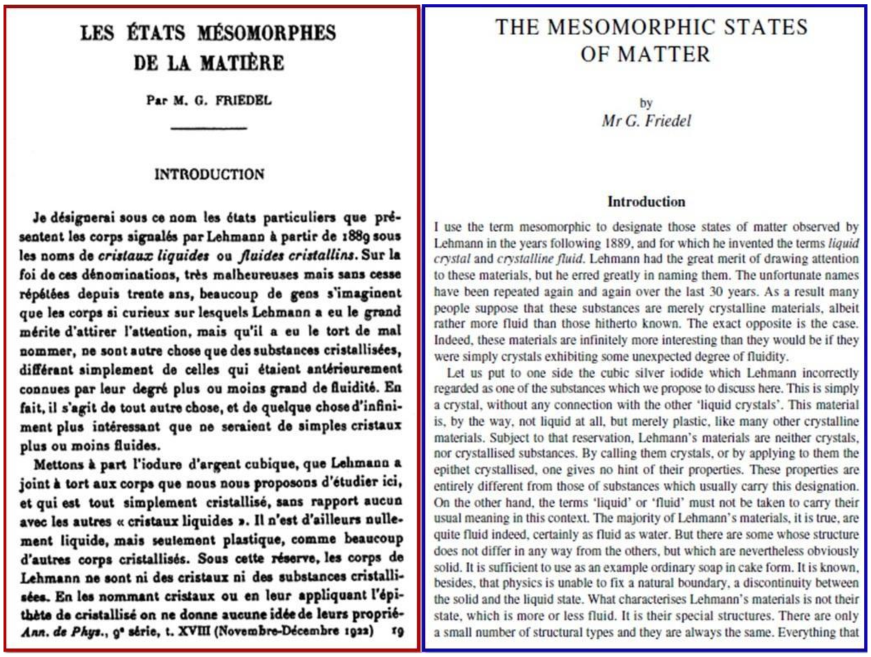
If a crystal really were a rigid molecular aggregate, a flowing crystal would indeed be as unlikely as flowing brickwork. However, if subject to sufficiently strong forces, even brickwork can be set into sliding motion. In a certain sense, the resulting motion corresponds to a stream of fluid mass in which the joints between the individual bricks open. The bricks then run out of control, moving over and rolling around each other in a disorderly manner, rather like single granules in a turbulent mass of sand.

As a matter of fact, there are solid – but nevertheless non-crystalline – bodies which are able to flow like liquids, although with much greater difficulty. This fact is evident to anyone who has ever observed the slow change of an unsupported stick of sealing wax or a larger free-standing mass of pitch. All fusable amorphous bodies transform from the liquid into the solid state continuously. The point at which the state of aggregation really becomes solid (i.e. where the first hints of the onset of displacement elasticity occur) is extremely difficult to recognise. Indeed, because such a material is still able to flow, we would often still regard it as fluid, even though, strictly speaking, it should already be described as solid.

Figure 8. O. Lehmann"s first article entitled "Flowing crystals" in Zeitschrift für Physikalische Chemie. The translation of the article from German to English was done by Prof Sluckin in his book [7].

Initially, liquid crystals were only known for their peculiarity which fetched no practical applications. But this took a turn when a lot of reports on compounds showing this character which quickly flourished the scientist to explore them for applications.

The term liquid crystals (Flussige Kristalle) was first used by Gattermann and Ritschke in the article "On Azoxy phenol ethers "(describes liquid crystalline properties of three compounds azoxy anisole, azoxy phenetole, and anisole azoxyphenetole)[8] . Early 20th century the German chemist by name Vorlander (1867-1941) started synthesizing many liquid crystalline samples and established quite well the synthetic designing aspect of new liquid crystalline materials. In 1922, Georges Friedel(1865-1933) a French mineralogist and crystallographer written a 200-page review article on liquid crystals ('Les États Mésomorphes de la Matiere' (i.e. 'Mesomorphic States of Matter') (**Figure 9**) where he gave a classification of different mesomorphic phases which are widely in use still. Swedish physicist by name George Oseen results on elastic properties of liquid crystals provided the basis of the continuum theory of liquid crystals which was proposed by Frank an English physicist. In 1927, Russian physicist Vsevolod Fridericksz (1885-1944) studied the effects of electric fields on the phase transitions of liquid crystals which was termed as Friedericksz transition.



LES ÉTATS MÉSOMORPHES
DE LA MATIÈRE

Par M. G. FRIEDEL

INTRODUCTION

Je désignerai sous ce nom les états particuliers que présentent les corps signalés par Lehmann à partir de 1889 sous les noms de *cristaux liquides* ou *fluides cristallins*. Sur la foi de ces dénominations, très malheureuses mais sans cesse répétées depuis trente ans, beaucoup de gens s'imaginent que les corps si curieux sur lesquels Lehmann a eu le grand mérite d'attirer l'attention, mais qu'il a eu le tort de mal nommer, ne sont autre chose que des substances cristallisées, différant simplement de celles qui étaient antérieurement connues par leur degré plus ou moins grand de fluidité. En fait, il s'agit de tout autre chose, et de quelque chose d'infiniment plus intéressant que ne seraient de simples cristaux plus ou moins fluides.

Mettons à part l'iodure d'argent cubique, que Lehmann a joint à tort aux corps que nous nous proposons d'étudier ici, et qui est tout simplement cristallisé, sans rapport aucun avec les autres « cristaux liquides ». Il n'est d'ailleurs nullement liquide, mais seulement plastique, comme beaucoup d'autres corps cristallisés. Sous cette réserve, les corps de Lehmann ne sont ni des cristaux ni des substances cristallisées. En les nommant cristaux ou en leur appliquant l'épithète de cristallisé on ne donne aucune idée de leurs proprié-

Ann. de Phys., 9e série, t. XVIII (Novembre-Décembre 1922) 19

THE MESOMORPHIC STATES
OF MATTER

by
Mr G. Friedel

Introduction

I use the term mesomorphic to designate those states of matter observed by Lehmann in the years following 1889, and for which he invented the terms *liquid crystal* and *crystalline fluid*. Lehmann had the great merit of drawing attention to these materials, but he erred greatly in naming them. The unfortunate names have been repeated again and again over the last 30 years. As a result many people suppose that these substances are merely crystalline materials, albeit rather more fluid than those hitherto known. The exact opposite is the case. Indeed, these materials are infinitely more interesting than they would be if they were simply crystals exhibiting some unexpected degree of fluidity.

Let us put to one side the cubic silver iodide which Lehmann incorrectly regarded as one of the substances which we propose to discuss here. This is simply a crystal, without any connection with the other 'liquid crystals'. This material is, by the way, not liquid at all, but merely plastic, like many other crystalline materials. Subject to that reservation, Lehmann's materials are neither crystals, nor crystallised substances. By calling them crystals, or by applying to them the epithet crystallised, one gives no hint of their properties. These properties are entirely different from those of substances which usually carry this designation. On the other hand, the terms 'liquid' or 'fluid' must not be taken to carry their usual meaning in this context. The majority of Lehmann's materials, it is true, are quite fluid indeed, certainly as fluid as water. But there are some whose structure does not differ in any way from the others, but which are nevertheless obviously solid. It is sufficient to use as an example ordinary soap in cake form. It is known, besides, that physics is unable to fix a natural boundary, a discontinuity between the solid and the liquid state. What characterises Lehmann's materials is not their state, which is more or less fluid. It is their special structures. There are only a small number of structural types and they are always the same. Everything that

Figure 9. G Friedel‟s the first article entitled "The Mesomorphic State of Matter". The translation of the article from German to English was done by Prof Sulckin in his book [9]

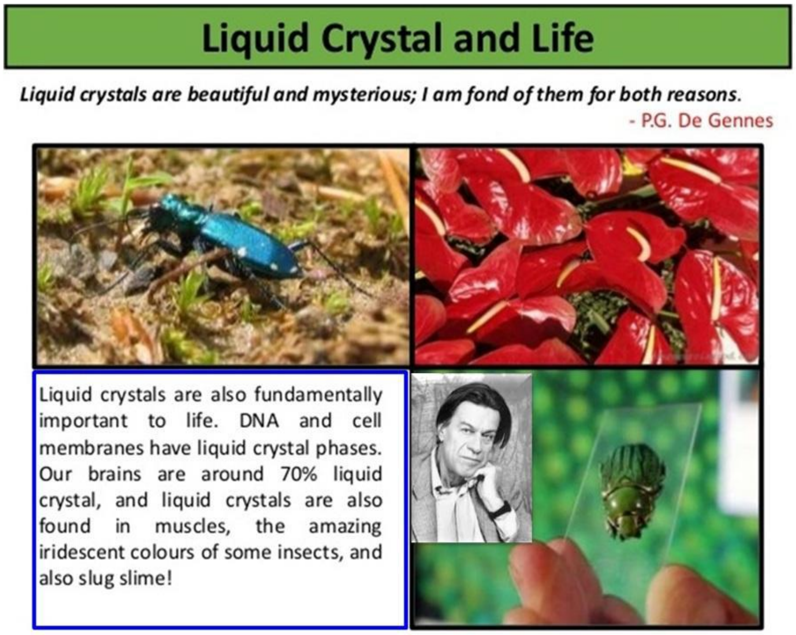
Figure 10. Pioneers of liquid crystal research. (a) Georges Friedel (1865–1933), (b) Vsevolod Fréedericksz (1885–1944), (c) George Heilmeier (1936–2014) and (d) Pierre-Gilles de Gennes (1932–2007).

Wilhelm Maier and his student Alfred Saupe a German scientist proposed a basic theory on liquid crystals which laid the basis for understanding the mesomorphic systems. In 1940s George Gray, Scottish organic chemist played a vital role in the systemization of liquid crystals by characterizing phases of various samples. His book on Molecular Structure and the Properties of Liquid Crystals published in 1962 serve as a bible for chemists and physicists around the globe for learning about designing new liquid crystalline molecules.

The scope of liquid crystal materials in display applications has urged people to design the room temperature mesogenic systems for effective use. The research on flat-panel displays started in the 1960s. The concept of Williams domains (appearance of stripe-like patterns as sample changing the alignment on the application of field discovered by Richard Williams (1927)). The discovery of Williams's domains stimulated the basis of pixels found in LCDs.

In the late 1960s, George Heilmeier (**Figure 10**) (1936–2014), discovered several new electro-optical effects in liquid crystals. He demonstrated 'dynamic scattering mode,' display which is known to be the first liquid crystal display. Heilmeier and his team are usually known to be associated with the invention of the liquid crystal display (see figure 1.2(c)).In the 1970s, Indian physicist Sivaramakrishna Chandrasekhar (1930–2004) introduced disc-shaped molecules to the liquid crystal research[10], In 1980, Chinese physicist Lui Lam (1944–), who showed the mesogenic potential of bowl-shaped molecules (called 'bowlics'). By the end of 1990, Liquid crystal research showed massive progress in terms of innovative applications apart from the display devices.

Dr. Tim Sluckin (university of Southampton), Prof D.A.Dunmur, Prof H.Stegemeyer together published an anthology consisting of preliminary communications on mesogenic systems entitled "Crystals that flow, classic papers from the History of Liquid crystals"[9]. They further published a text book on liquid crystals by title "Soap, Science and Flat screen TVs" which gives the beautiful account on the history of liquid crystals in display applications [11]. The field of liquid crystal research has come a long way since the observation of Reinitzer. One of the notable recognition for liquid crystal research was due to the award of Nobel Prize to French physicist Pierre de Gennes (1932–2007) for his contribution towards the development of methods to study the ordering in condensed matter systems in particular liquid crystals and polymers (**Figure 11**).



Liquid Crystal and Life

Liquid crystals are beautiful and mysterious; I am fond of them for both reasons.

- P.G. De Gennes

Liquid crystals are also fundamentally important to life. DNA and cell membranes have liquid crystal phases. Our brains are around 70% liquid crystal, and liquid crystals are also found in muscles, the amazing iridescent colours of some insects, and also slug slime!

Figure 11. P.G.De Gennes and his noble prize

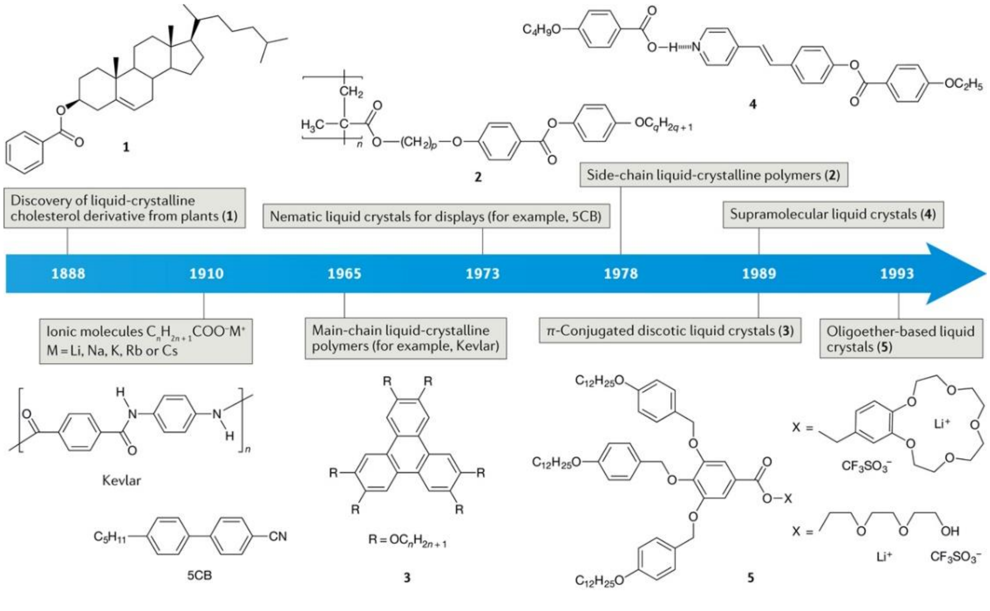


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Figure 12. History of liquid crystals-Timeline chart[12]

1.4 Classification of liquid crystals:[13]

Liquid crystals are classified on the basis of several aspects as follows

1. Classification based on the degree of positional order
2. Classification based on the mechanism of transition
3. Classification based on shape
4. Classification based on molar mass
5. Classification based on the symmetry

1.4.1 Classification based on the degree of positional order:[14]

Depending on the degree of positional order, we can classify the liquid crystalline phases as follows

1.4.1.1 Nematic phases:

The nematic phase has a high degree of long-range orientational order of the molecules, but no long-range positional order. This is the least ordered mesophase (closest to the isotropic liquid state) (**Figure 13**). It differs from the isotropic liquid in that the molecules are spontaneously oriented with their long axes approximately parallel to the preferred direction of orientation of the molecules, depicted as a long arrow, and is called the *director*. The word nematic is a Greek word meaning thread because they often show thread-like structures under the polarizing microscope.

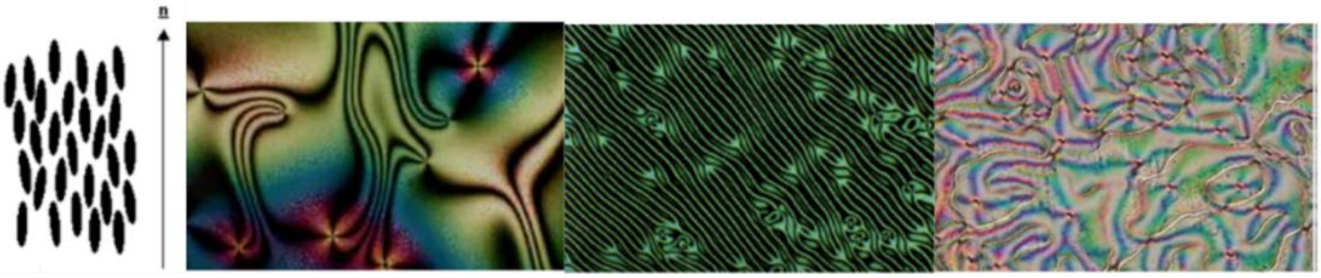

Figure 13. Arrangement and POM texturs of Nematic phase

There is a special class of nematic liquid crystals called chiral nematic (**Figure 14**) . Chiral refers to the unique ability to selectively reflect one component of circularly polarized light. The term chiral nematic is also known as a cholesteric phase. Because it was first observed in cholesterol derivatives.

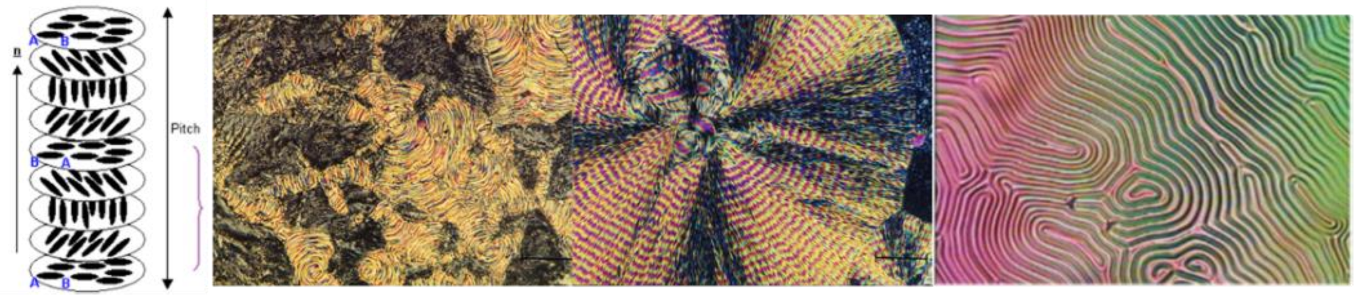

Figure 14. Arrangement and POM texturs of cholesteric phase

1.4.1.2. Smectic phases:

Molecules in this phase show a one-dimensional positional order. In the smectic state, the molecules maintain the orientational order as that of nematics and have the tendency to align themselves in layers. In the smectic-A mesophase, the director is perpendicular to the smectic plane, and there is no particular positional order in the layer (**Figure 15**). Similarly, the smectic-B mesophase orients with the director perpendicular to the smectic plane, but the molecules are arranged into a network of hexagons within the layer. In the smectic-C mesophase, molecules are arranged as in the smectic-A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane. The word "smectic" is derived from the Greek word for soap as these kinds of phases were first found in soaps.

Figure 15. Arrangement and POM textures of Smectic phase

1.4.1.3 Columnar phases:

The columnar phases were known to have two-dimensional positional order where molecules assemble into cylindrical structures. These liquid crystals were initially termed as discotic liquid crystals because they are often shown by flat disc-shaped molecules. But there are various reports of columnar liquid crystals exhibited by non-discotic molecules. Columnar liquid crystals can be further classified according to the packing arrangement of the columns. The detailed account on these types will be discussed later in this chapter. (**Figure 16**)

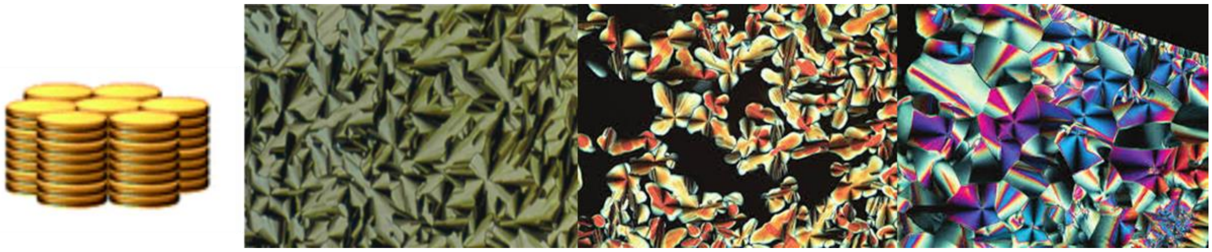

Figure 16. Arrangement and POM textures of the columnar phase

1.4.2 Classification according to the mechanism of transition:[15]

Liquid crystals can be classified according to their mode of formation into three types

1.4.2.1 Thermotropic liquid crystals

Thermotropic liquid crystals are a class of liquid crystals that show mesomorphism with the application of heat. These materials are generally associated with two-phase transitions as a function of temperature (Figure 17 & Figure 18). The melting and clearing points, the degree of ordering decreases in each phase as the temperature is increased. Along with the geometric anisotropy, interaction anisotropy and microsegregation are the driving parameters for mesophase formation

- **Melting point (T_m):** The transition from the crystalline solid to the liquid crystal phase or isotropic phase. (Figure 18)

- **Clearing point (T_c):** The transition from the liquid crystal to isotropic phase (**Figure 17**)

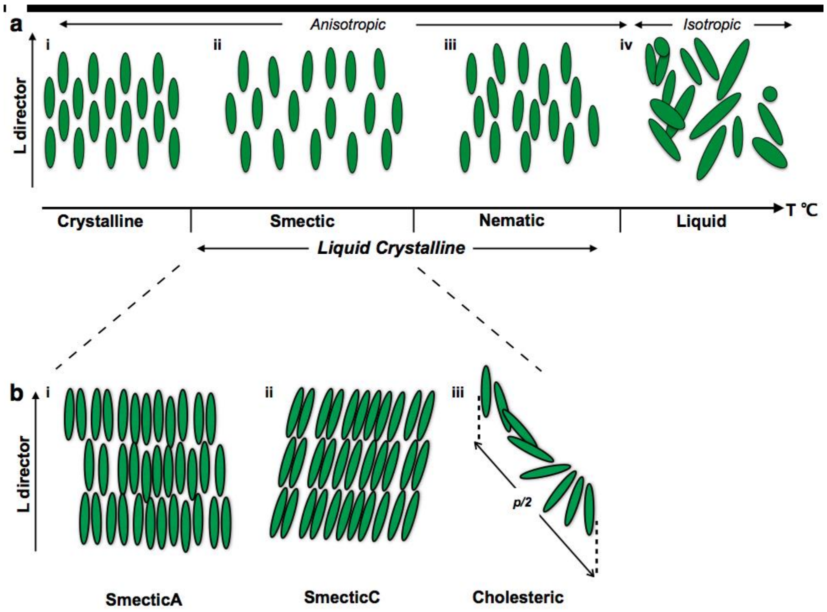

Figure 17. Phase transitions in thermotropic liquid crystals

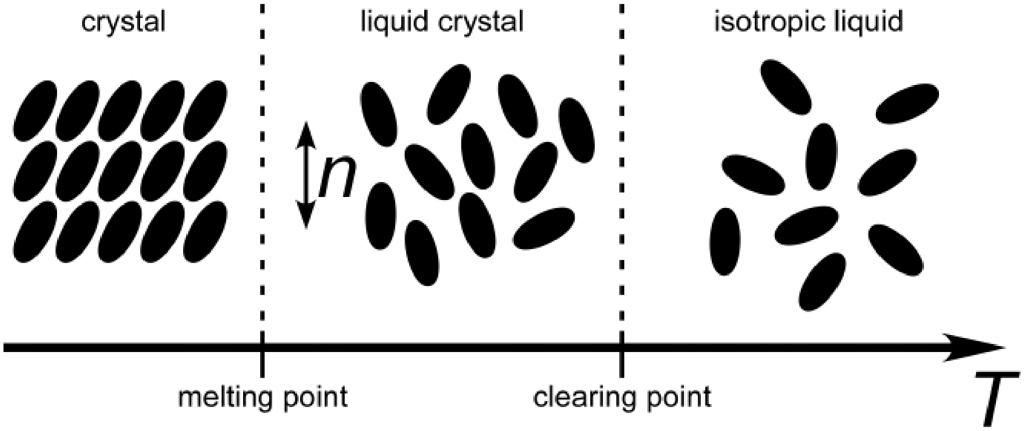

Figure 18. Phase transitions in thermotropic liquid crystals

Thermotropic systems can further classified into two types as follows (**Figure 18**)

Enantiotropic liquid crystals: An enantiotropic phase transition is the one that occurs above the melting transition such that the phases involved are thermodynamically stable.

Monotropic liquid crystals: Monotropic phase transition is one that occurs below the melting point, where at least one of the phases exists only at temperatures below the melting point and is revealed by the supercooling of the material.

1.4.2.2 Lyotropic liquid crystals: Lyotropic liquid crystals are composed of molecules with amphiphilic properties dissolved in a solvent. The amphiphilic compounds are constituted by two distinct parts of contrasting behavior, a hydrophilic polar “head” and a hydrophobic nonpolar “tail”. Mesophase formation in lyotropic liquid crystals is controlled by concentration and /or temperature. Typical examples of lyotropic liquid crystals are soaps in water and

Various phospholipids. There are various types of lyotropic mesophases. Each of these different types has a different extent of molecular ordering within the solvent continuum. Detailed account on lyotropic systems are given later in this chapter.

1.4.2.3 Amphotropic liquid crystals: Substances which show both thermotropic and lyotropic behavior are called amphotropic liquid crystals. This term was derived from Amphi (meaning both, of both kinds); and -tropic (meaning that which turns, turn direction).[16]

1.4.3 Classification based on molar mass:[17]

The most common liquid crystal systems reported are the small organic molecules comprised of anisotropy involving rigid aromatic units with end flexible chains. These can be termed as monomeric liquid crystals. However, polymer chemistry research has exhibited that certain systems of high molar mass (i.e. Polymers) display the liquid crystalline behavior. These mesogenic polymer systems have been termed as ‘polymer liquid crystals’ (PLC);

Polymer liquid crystals can be classified into different types

1.4.3.1 Main chain liquid crystal polymers (MCLCPs)

- Contains repeating units which are mesogenic themselves
- The monomeric unit need to be bifunctional in order to have scope of polymerization
- The monomeric unit should be anisotropic.

- They are constructed by linking together appropriate monomer mesogens into a polymer backbone
- Depending on the monomers, the backbone may be comprised of alternating rigid and flexible segments (**Figure 19**)
- Common industrial applications of main-chain polymers include the polyolefins and polyacrylates, polymethacrylates.

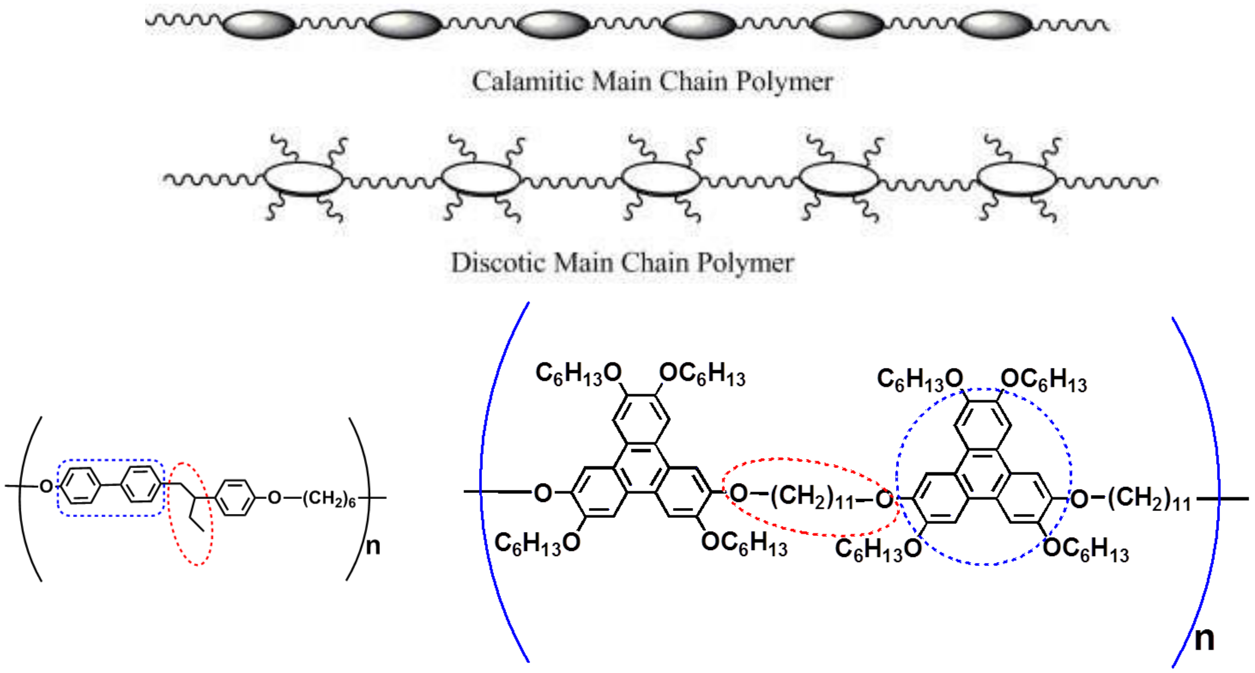

Figure 19. Schematic and examples of main-chain liquid crystal polymers

1.4.3.2 Side-chain liquid crystal polymers (SCLCPs)

- When the mesogenic monomers contain end-chains that can polymerize themselves leads to backbone results in the mesogenic cores dangling from the backbone as a side chain.
- The crucial consideration in predicting the properties of a side-chain polymer liquid crystalline material is the rigidity of the core linkage to the backbone.
- The mesogenic units are invariably separated from the polymer backbone by fairly long spacer units which are usually several methylene units or ester units of ether units at the point of attachment (**Figure 20**)

- Direct, or rigid, linkage hinders the formation of liquid crystalline phases and in general only an uninteresting anisotropic structure results, which vanishes at the ‘glass transition.
- When a flexible spacer or linkage group is present, the backbone motions do not prevent the side-chain cores from arranging themselves anisotropically which leads to mesogenicity

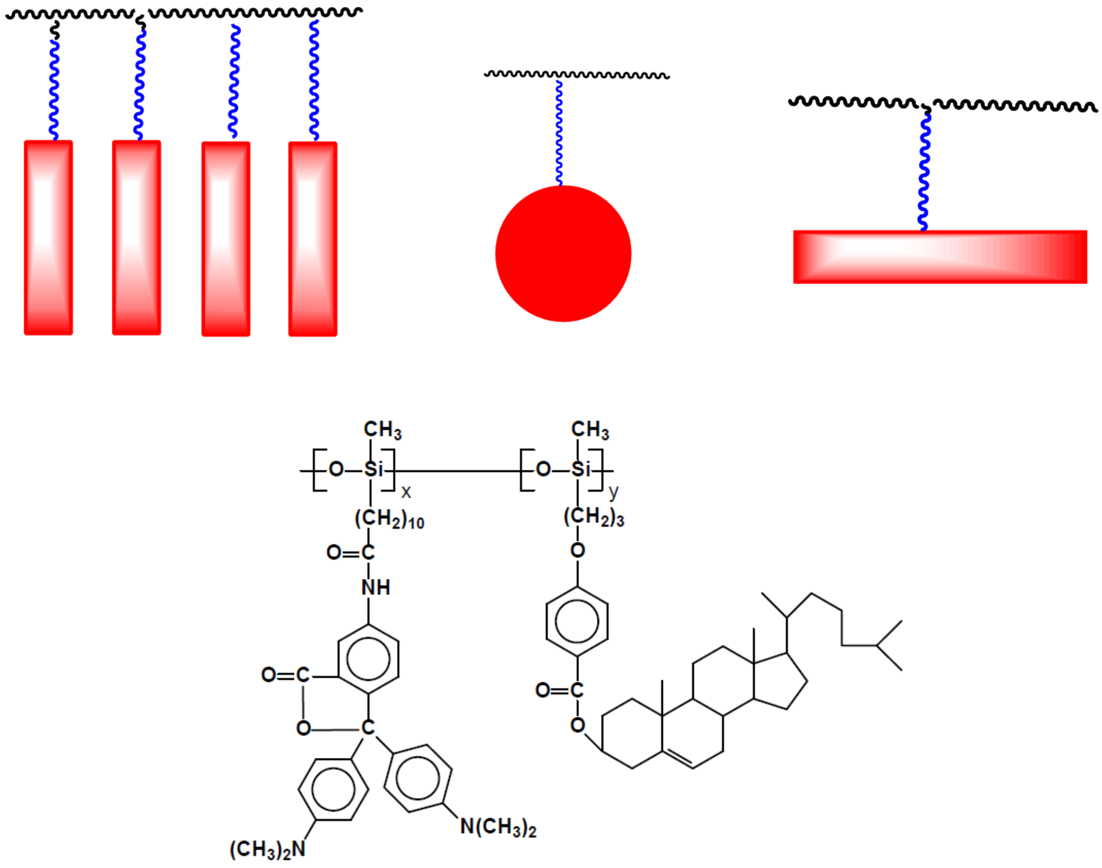

Figure 20. Schematic and examples of side-chain liquid crystal polymers

1.4.3.3 Combined liquid crystal polymers:

- Combines the characteristics of both main chain and side-chain polymers.
- Side- chain mesogenic motifs can be attached to main chain mesogenic polymer through a spacer to the mesogenic main chain at the linking unit or mesogenic unit (**Figure 21**)

- In between the low molar mass monomeric and high molar mass polymer LCs there exist monodisperse LC dimers, trimers, higher oligomers and dendrimers which have served as the model compounds to understand the transitional properties of LC polymers

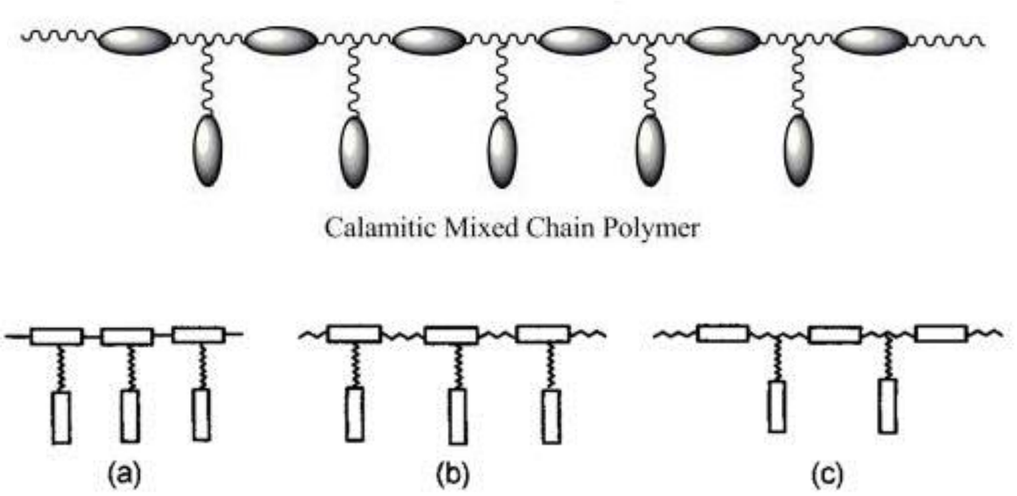

Figure 21. Schematic of Mixed chain liquid crystal polymers

1.4.4 Classification based on the symmetry:

This mode of classification is not widely known. The molecules are classified on the basis of point group symmetry of mesogens. The detailed explanation of this classification will be outside the scope of this chapter. The detailed account can be found in the handbook of liquid crystals[18].

1.4.5 Classification based on shape:

This mode of classification is widely followed by the research community. Based on the shape of the mesogens. Thermotropic liquid crystals are classified into three main groups:

(a) Calamitic (rod-like);

(b) Discotic (disc-like), and

(c) Bent core (banana-like).

1.4.5.1 Calamitic (Rod-like) liquid crystals:[2]

Rod like molecules forms the most common type of molecules reported for mesophase character. The rod-like molecules or calamitics generally possess an elongated shape. These molecules have molecular length (l) is much greater than the molecular breadth (b) (**Figure 22**). The anisotropy associated with shape in addition to interaction anisotropy (induced by incompatibility due to the nature of different constituents in the molecular structure). The structure of calmitics involving two or more ring structures that are bonded either directly or through spacers linking groups. Further, they are generally functionalized with terminal alkoxy chains or alkyl chains. Further, the influence of lateral substituents in the rings plays a vital role in deciding the mesophase character. Calamitics generally show nematic or smectic phases.

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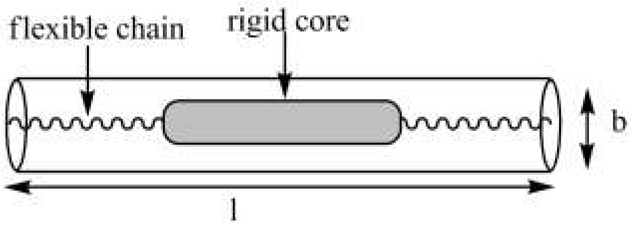

Figure 22. Schematic of calamitic Liquid crystals

The typical chemical structure of these molecules can be represented (**Figure 23**) by the general template**.**

A and B - core units (benzene, naphthalene, biphenyl, etc.),

R , R' - Flexible moieties includes normal and/or branched alkyl groups,

M , N - small lateral substituents (-X, $-NO_2$, $-CH_3$, $-OCH_3$, -CN, etc.).

Y -linking group to the core units

Mesophase morphology and physical properties are generally dependent on lateral substituents

X , Z - linking groups of terminal chains and core units.

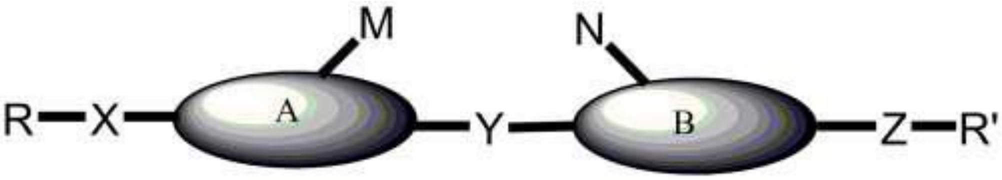

Figure 23. General chemical structure of calamitic Liquid crystals

Generally, calamitics show the following two phases (**Figure 24**)

1. Nematic (from Greek word *nematos* meaning "thread"),
2. Smectic (from the Greek word *smectos* meaning "soap") etc. depending on the arrangement of the mesogens in different mesophase

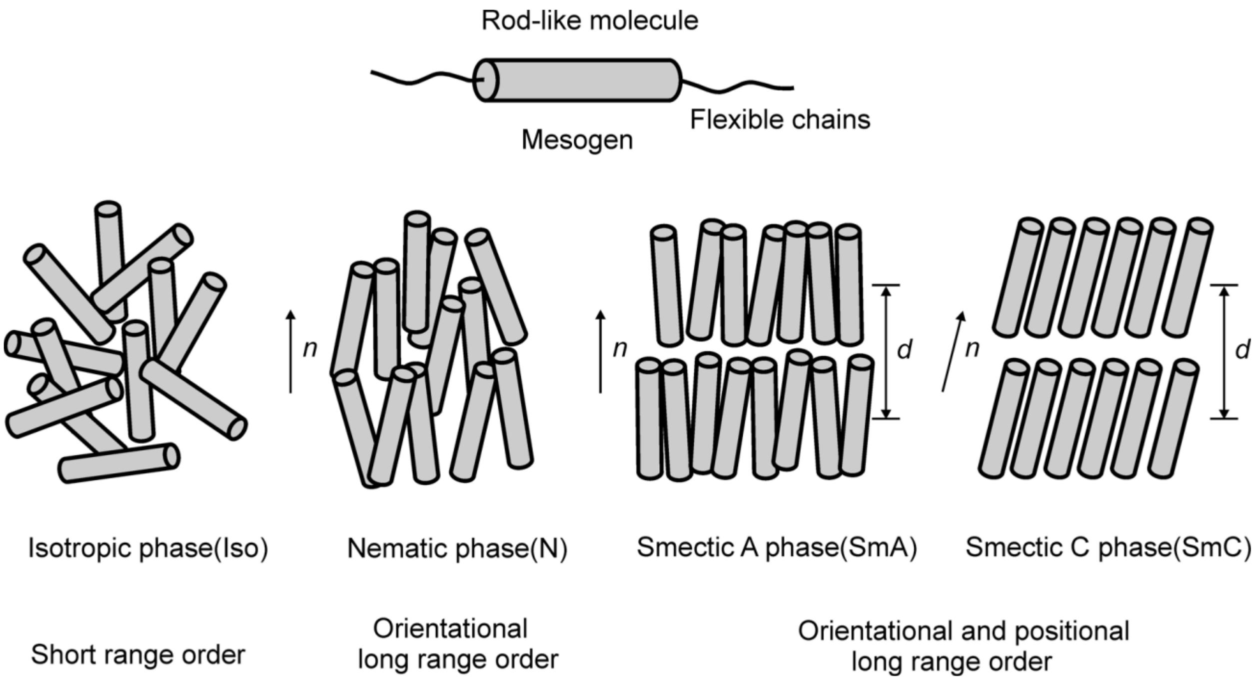

Figure 24. Phases of calamitic liquid crystals

1.4.5.1.1 Nematic phase: The nematic phase has a high degree of long-range orientational order of the molecules, but no long-range positional order. This is the least ordered mesophase (closest to the isotropic liquid state). It differs from the isotropic liquid in which the molecules are spontaneously oriented with their long axes approximately parallel. The preferred direction of orientation of the molecules, depicted as a long arrow, is called the *director* (**Figure 25**).

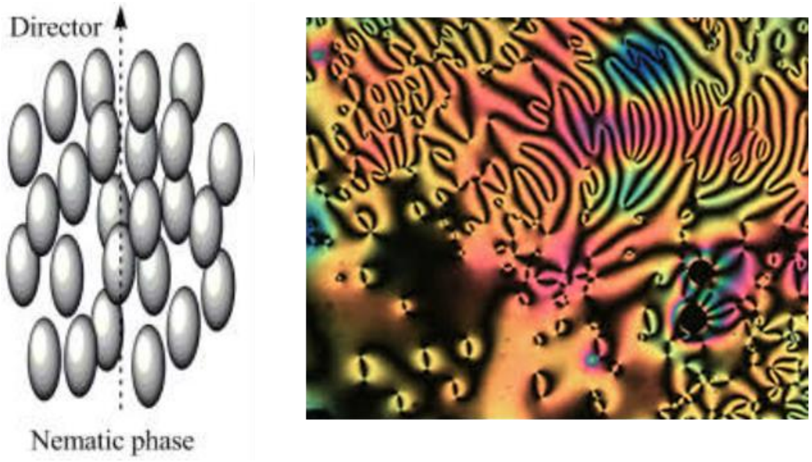

Figure 25. Nematic Phases of calamitic liquid crystals

1.4.5.1.2 Smectic phase: The word "smectic" is derived from the Latin word ″smecticus". Which means soap or having soap-like properties. Molecules in this phase show additional degrees of positional order not present in the nematic phase. In the smectic phase, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers; with a well-defined interlayer spacing, which can be measured by X-ray diffraction (**Figure 26**).

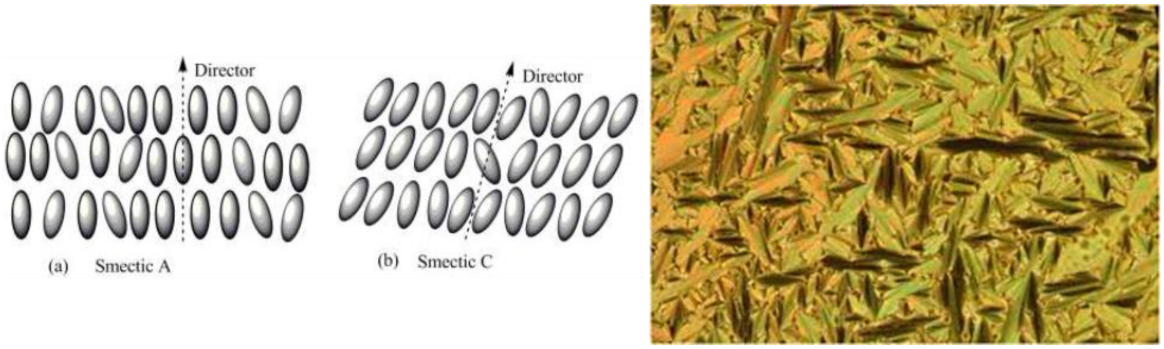

Figure 26. Smectic Phases of calamitic liquid crystals

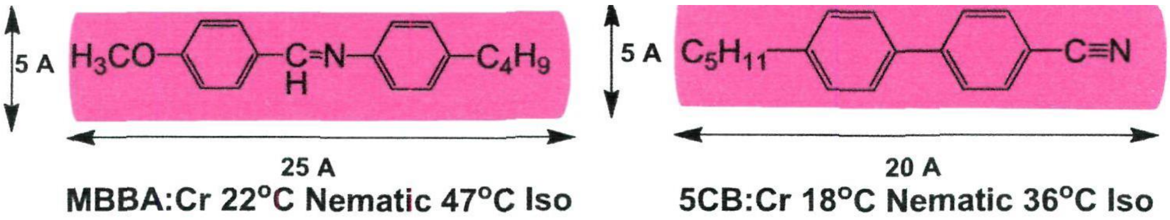

Figure 27. Examples of calamitic liquid crystals

1.4.5.2 Bent core liquid crystals[19]:

The molecules with bent shapes can be thought of as two rods connected at an angle leading to bent shape that has been found to show the mesomorphic potential. These bent-core mesogens were most recent among the other class of liquid crystals. These bent systems were found to show nematic and smectic phases as similar to their calamitic counterparts. They were found to show a special phase called bent phases which are numbered in the chronological manner (B1 to B8). Bent or bow-shaped mesogens are famous for their ferroelectric behavior. The general structure variations and dimers and their representative POM images are shown in **Figure 28 & Figure 29**.

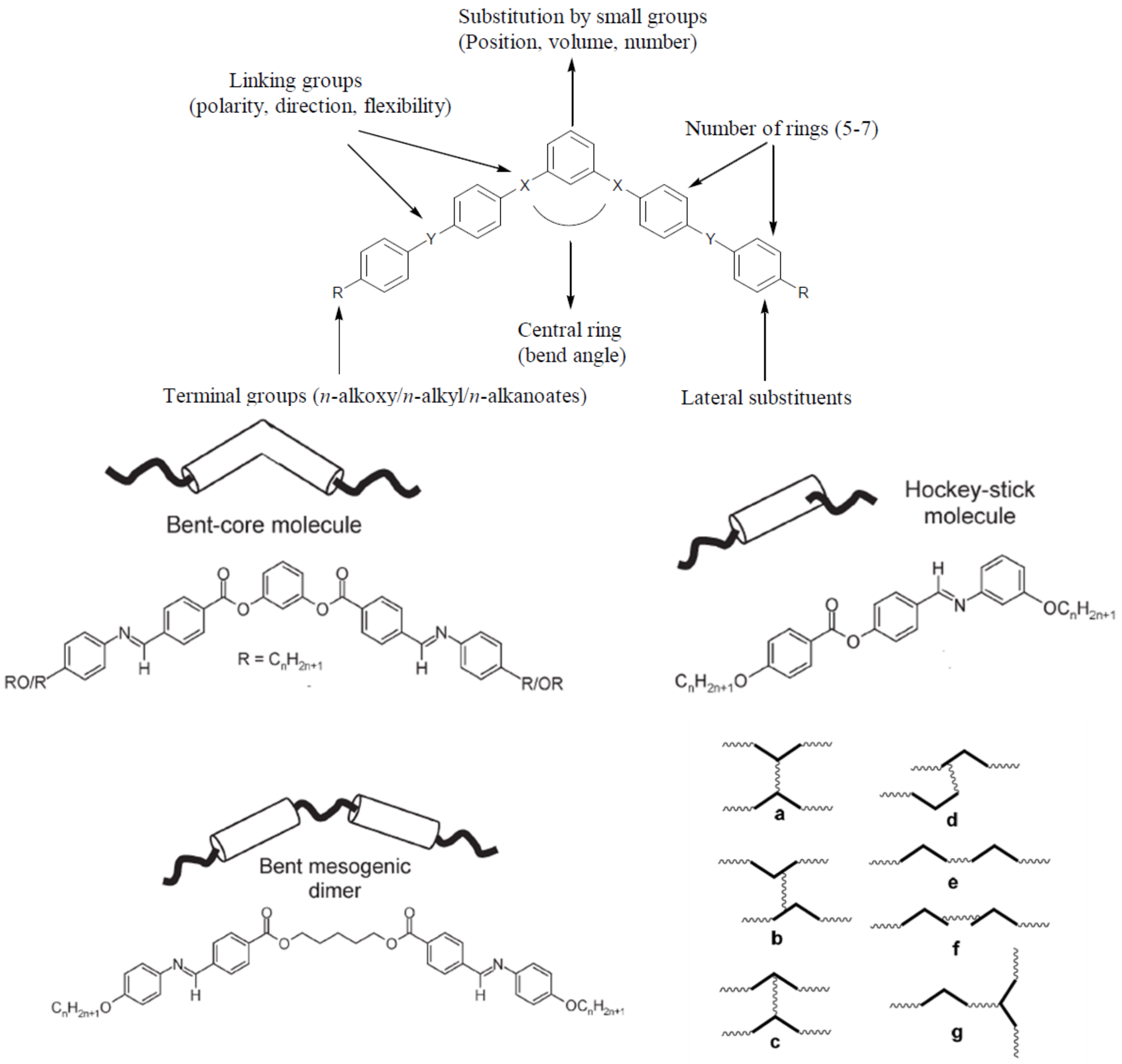

Figure 28. The general structure of bent-core liquid crystals

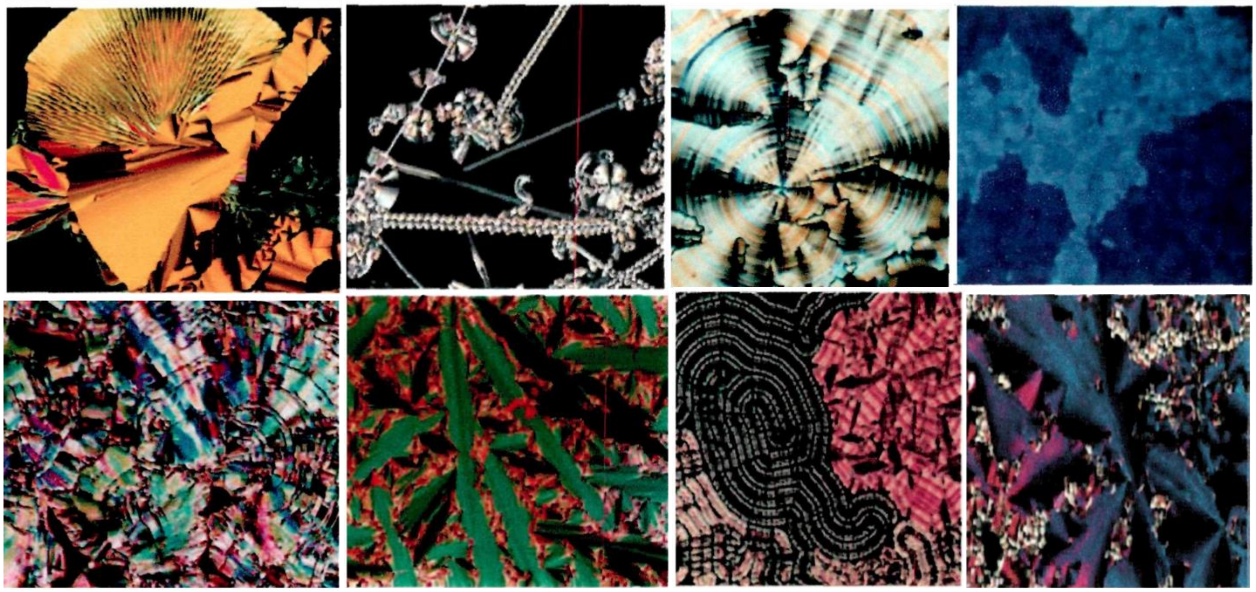

Figure 29. POM images of B (B1-B8) phases shown by bent-core liquid crystals

1.4.5.3 Discotic liquid crystals[20]:

1.4.5.3.1 The advent of discotic liquid crystals:

The possibility of the mesomorphic potential of disc-shaped systems started in 1923[21]. Vorlander (**Figure 30**) one of the pioneers in liquid crystal research suggested the idea of disc-based systems with the packing arrangement similar to voltas columns on analyzing triphenylene and perylene. He was not able to observe any mesomorphic signatures probably because the molecules, he studied were lacking flexible chains. Further, he mentioned in his article that leaf-shaped molecules do not form any liquid crystals at all. But later triphenylenes and perylenes with flexible periphery were found to constitute major reports in discotic literature[22].

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Figure 30. Pioneers of discotic liquid crystals ((from left to right), Prof. Vorlander, Prof. S. Chandrashekar, Prof.B.K.Sadashiva, Prof.K.A.Suresh)

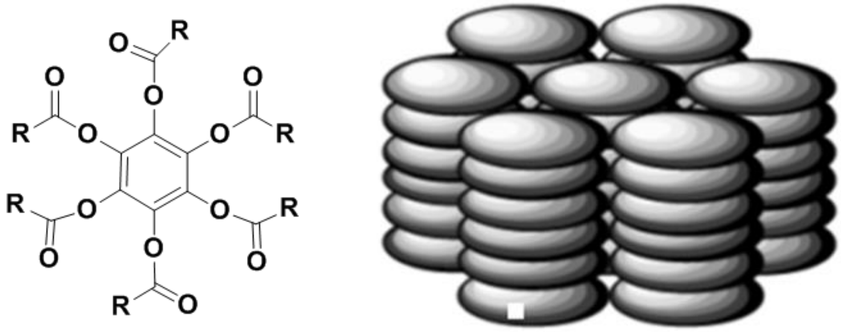
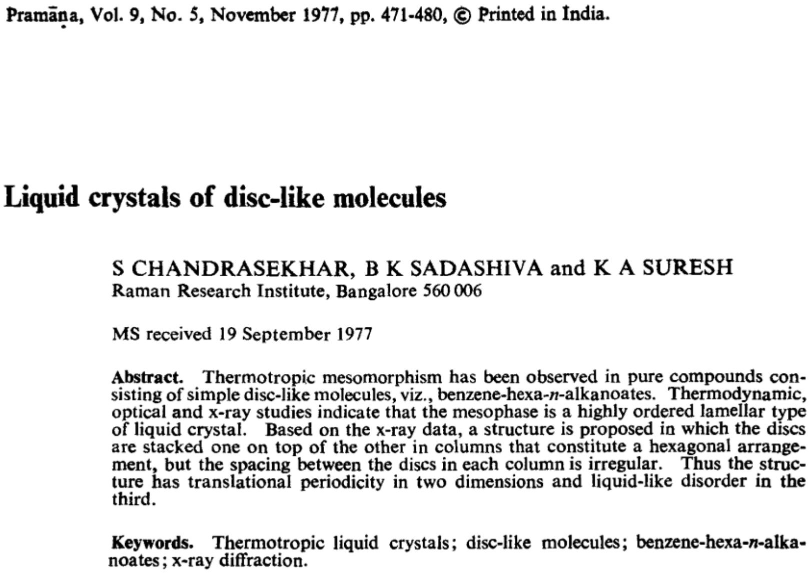


Figure 31. Benzene-Hexaalkanoates- First discotic compound

In September 1977, Sivaramakrishna Chandrasekhar and his colleagues at The Raman Research Institute reported: "…*what is probably the first observation of thermotropic mesomorphism in pure, single-component systems of relatively simple plate-like, or more appropriately disc-like* *molecules*”. They confirmed the mesophase behavior of benzene hexa-*n*-alkanoates (**Figure 31**) through thermodynamic, optical and X-ray studies. They established that these flat-shaped molecules stacked one on the top of other in columns that constitute a hexagonal arrangement. This report shown the world a new fascinating field of liquid crystal research. (**Figure 32**)



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Liquid crystals of disc-like molecules

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MS received 19 September 1977

Abstract. Thermotropic mesomorphism has been observed in pure compounds consisting of simple disc-like molecules, viz., benzene-hexa-*n*-alkanoates. Thermodynamic, optical and x-ray studies indicate that the mesophase is a highly ordered lamellar type of liquid crystal. Based on the x-ray data, a structure is proposed in which the discs are stacked one on top of the other in columns that constitute a hexagonal arrangement, but the spacing between the discs in each column is irregular. Thus the structure has translational periodicity in two dimensions and liquid-like disorder in the third.

Keywords. Thermotropic liquid crystals; disc-like molecules; benzene-hexa-*n*-alkanoates; x-ray diffraction.

Figure 32. First report n discotic liquid crystals[10]

Brooks and Taylor, in the 1960 s gave a brief research account on liquid crystalline behavior of these materials when graphitizable substances on pyrolysis, led to nematic textures which were called as carbonaceous mesophases. These carbonaceous phases were believed to be made up of flat poly aromatic motifs, not by organic molecules which eliminated the feasibility of complete characterization. But they were homogenous and stable. The self-organization of these disc-shaped molecules was found to be unique in terms of their self-assembly behavior in the mesophase. They proposed a model for the layer organization of pyrolytic graphites. The carbonaceous mesomorphic behavior of this pyrolytic graphite can be thought of as similar to graphenes and polycyclic aromatic systems which are widely known for their semiconducting nature comparable to that of silicon (**Figure 33**). After the report of benzene based discotic, French research groups reported columnar behavior shown by other disks like molecules.

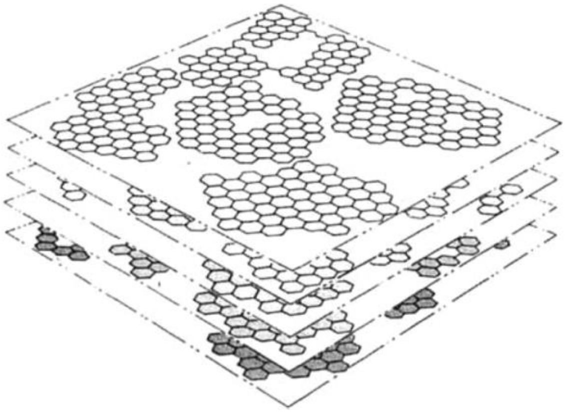


Figure 33. Fist report on carbonaceous mesophase.

Discotic molecules have the potential to self-organize spontaneously in a form of 1D columns, i.e; they can repair the structural defects inside self-assembling structures. (**Figure 34**)

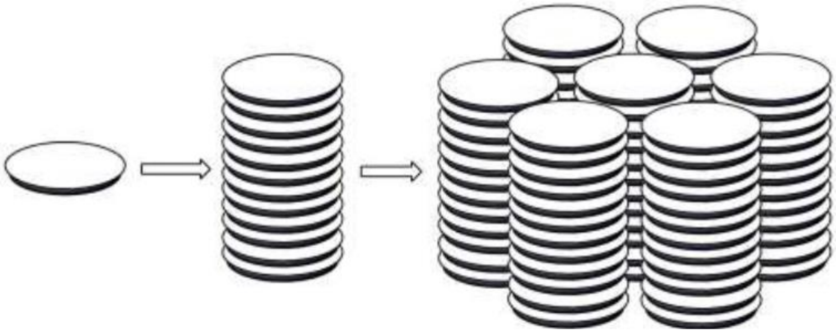


Figure 34. Schematic for the formation of columnar phases

DLCs are very famous for their columnar order which can be attributed to intense $\pi - \pi$ interactions of fused aromatic cores. The core-core separation in a columnar mesophase is usually of the order of 3.5 Å. This implies that there is a considerable overlap of p-orbitals. The length of flexible tails surrounding the core decides the intercolumnar distance which is usually around 20-40Å. The above values suggest that the interactions of molecules within the same column are much stronger than interactions between the columns. This diverse nature of interactions among the columns suggests the charge migration in these materials to be quasi one- dimensional in nature. This has been proved by analyzing the conductivity values along the column with the conductivity at the perpendicular direction (**Figure 35**). This anisotropic conductive nature of discotic columns inspired the scientist to call these materials as the molecular wires. Thus the columns may be described as molecular wires. The self assembles structures of discotic materials showed great semiconducting behavior which makes them one of the potential candidates to be employed in LEDs transistors, solar cells, etc.

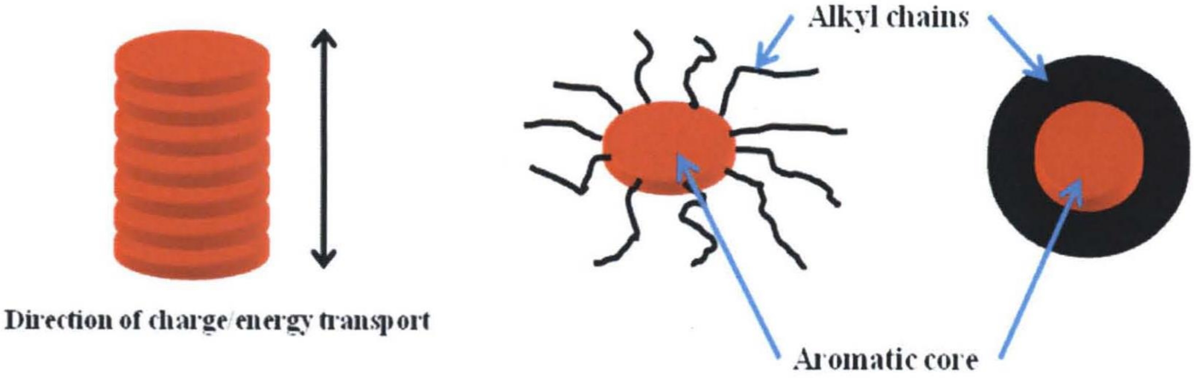


Figure 35 Anisotropic conductivity in discotics

1.4.5.3.2 General Structure for Discotic Liquid Crystals

The molecules forming discotic liquid crystals are generally composed of a central Disc-like core (such as benzene, triphenylene, truxene) and around the central core 3 to 12 saturated peripheral chains of three or more carbon atoms are substituted (**Figure 36**).

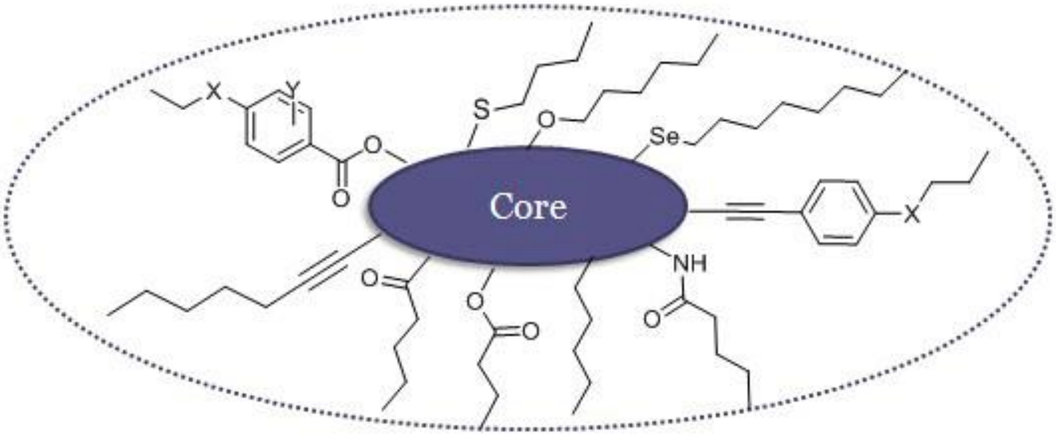


Figure 36. General schematic of a discotic mesogen

Discotic liquid crystals can be classified further depending on the nature of cores reported

1. Carbocyclic
2. Heterocyclic

Carbocyclic discotic liquid crystals (**Figure 37**) are those where the central core is completely made up of carbon and hydrogen. Mostly the discotics made from these core are usually electron donating in nature. (Figure 37)

Heterocyclic discotics liquid crystals (**Figure 38**) are those materials where the central core contains atoms such as N, S, O, P, Se, and B apart from carbon and hydrogen. These compounds are usually electron deficient in nature. (Figure 38)

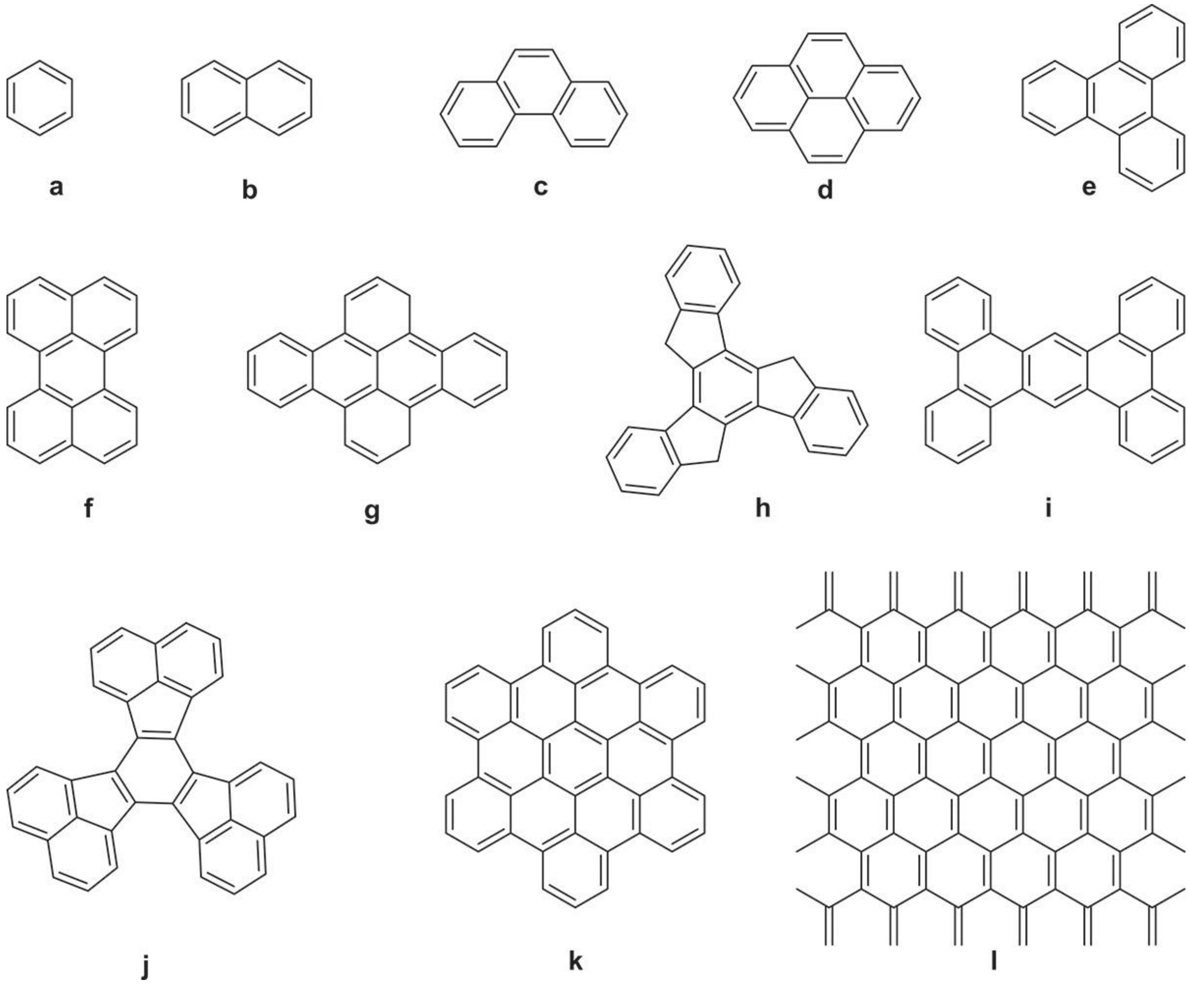


Figure 37. Carbocyclic Discotic cores reported in literature

Examples of reported heterocyclic discs: (a) Benzene; (b) Napthalene; (c) Phenanthrene; (d) Pyrene; (e) Triphenylene; (f) Perylene; (g) Dibenzopyrene; (h) Truxene; (i) Dibenzoanthracene; (j)Decacyclene ;(k) Hexabenzocoronene; (l) Graphene;

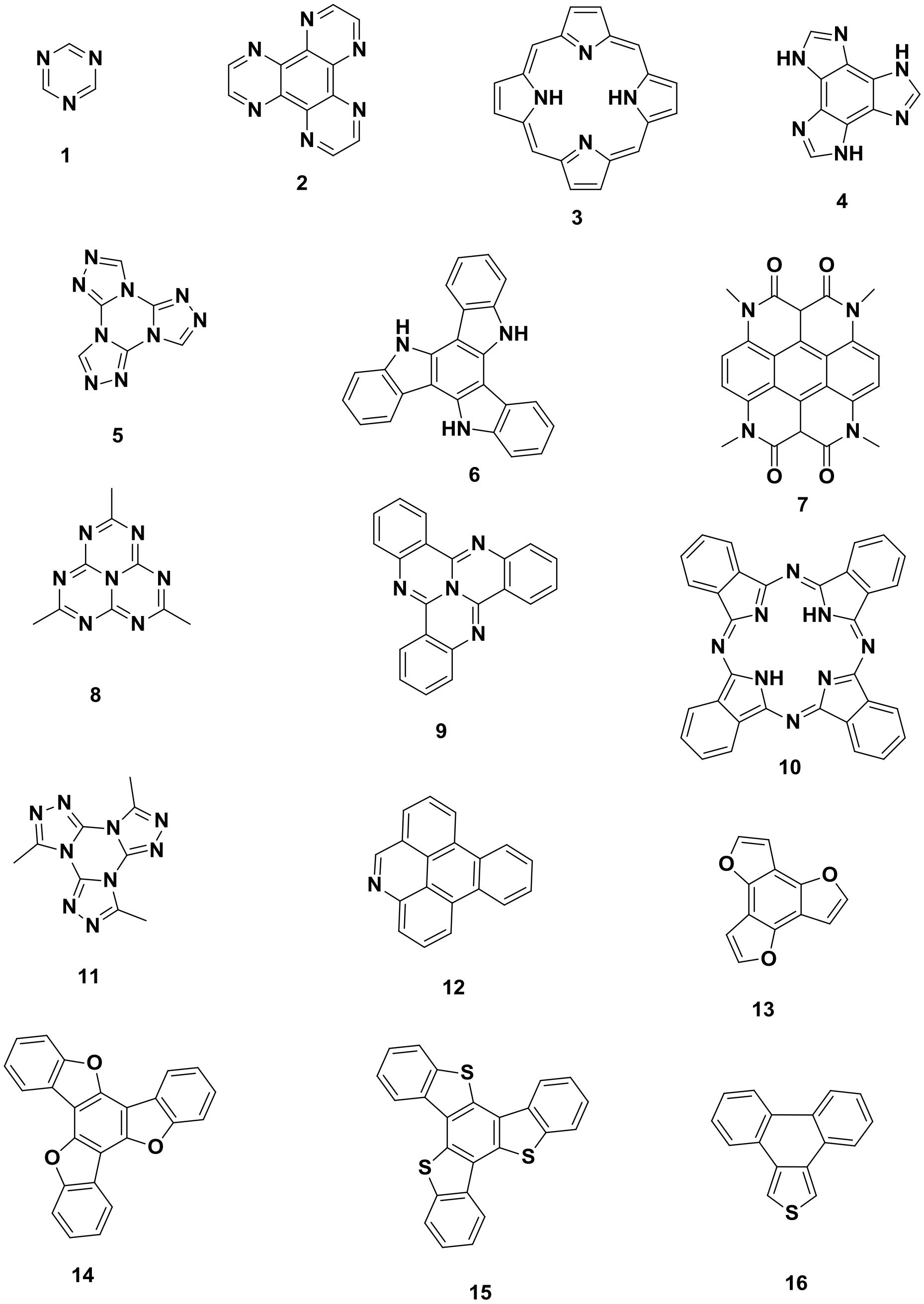


Figure 38. Heterocyclic Discotic cores reported in the literature

Examples of reported heterocyclic discs: (1) Triazine; (2) Quinoxaline; (3) Porphyrin; (4) Benzotrriimidazole;(5) Tris triazlotriazine; (6) Triindole; (7) Hetercoronenes; (8) Heptazine; (9) Tricycloquinazoline; (10)Phthalocyanine;(11) Triazolotriazine; (12) Azacoronene; (13)Benzotrifuran; (14)Benzotrisfuran; (15) Benzotrithiophene; (16)Phenathrothiophene

1.4.5.3.3 Structure of the liquid crystalline phases formed by discotic mesogens

Generally, a discotic molecule shows only one mesophase. The reports on polymorphism in discotics is countable in number. Discotics have been reported to form the following four types of phases (**Figure 39**).

1. Nematic phases
2. Columnar phases
3. Smectic phases
4. Cubic phases

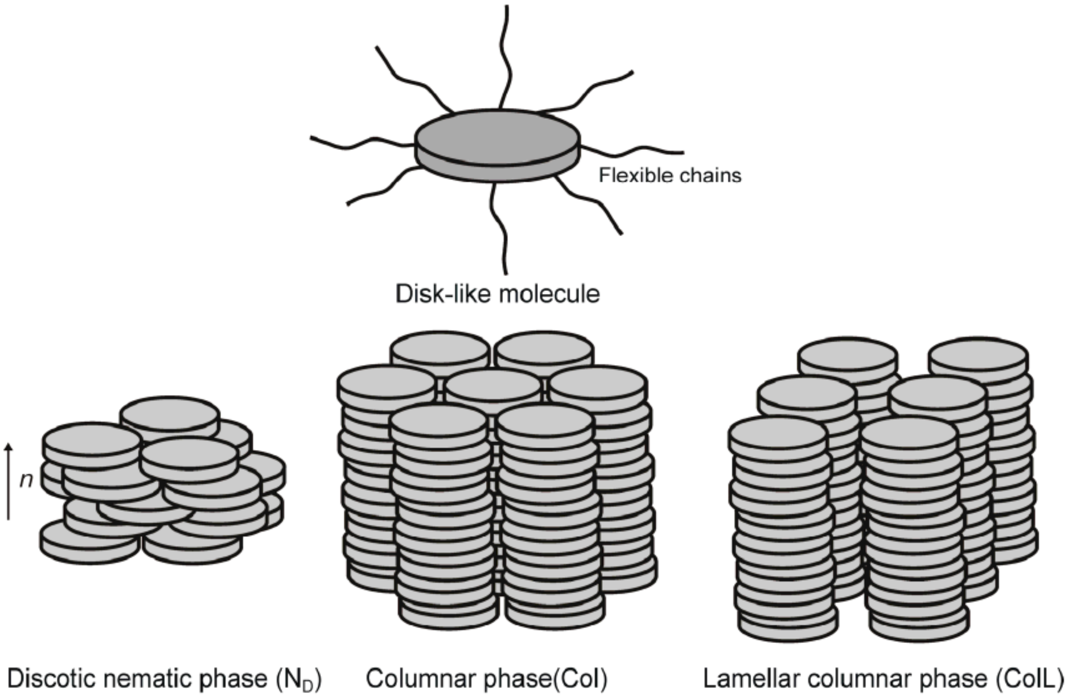


Figure 39. Types of Mesophases reported on discotics

1.4.5.3.3.1 Nematic Phases of discotic mesogens:[23]

The nematic phase shown by disc-shaped mesogens can be categorized into four types based on the molecular arrangement (**Figure 40**)

a. Discotic Nematic (N_D)
b. Chiral Nematic (N_D*)
c. Columnar Nematic (N_{col})
d. Nematic Lateral (N_L)

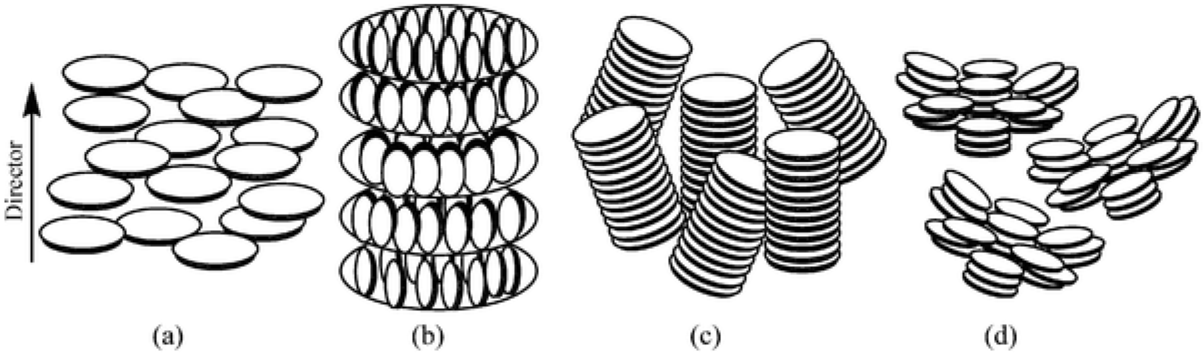


Figure 40. Nematic phases shown by disc molecules : (a) Discotic nematic; (b) Chiral neamtic; (c) Columnar Nematic ; (d) Lateral Nematic

a. **Discotic Nematic phases (N_D): (Figure 41)**

   - Molecules possess orientational order due to their parallel arrangement but they lack long-range positional order (figure 41)
   - These nematic phases are generally not miscible with the nematic phase exhibited by calamitics however both of them belong to the same symmetry
   - The director is along the short molecular axis of the molecule

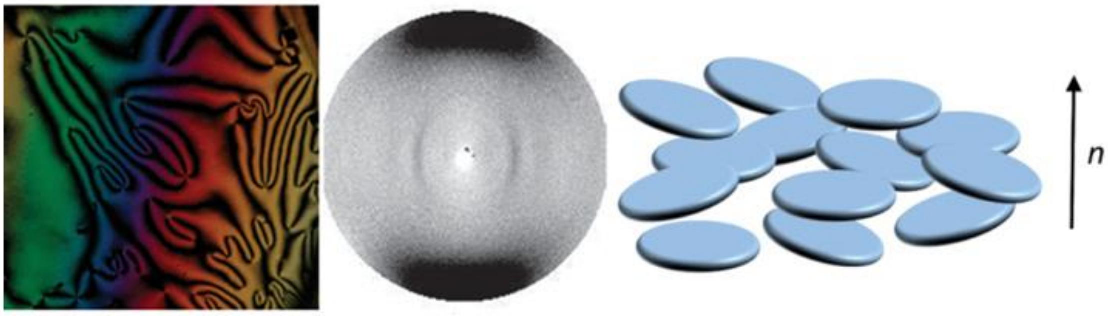


Figure 41. POM image, Diffraction pattern, and arrangement of N_D phase

b. **Chiral Nematic (N_D*)**

   - Similar to cholesteric phase chiral discotic nematic also exists
   - Usually induced in mixtures of a discotic nematic molecule with chiral dopants (can be mesomorphic or not)

- This phase is usually characterized by the helical structure

c. Columnar Nematic (N_{col}) (Figure 42)

- This phase is always characterized by columnar stacking of molecules
- The column does not lead to any two-dimensional structures
- Possess short-range positional order with long-range orientational order

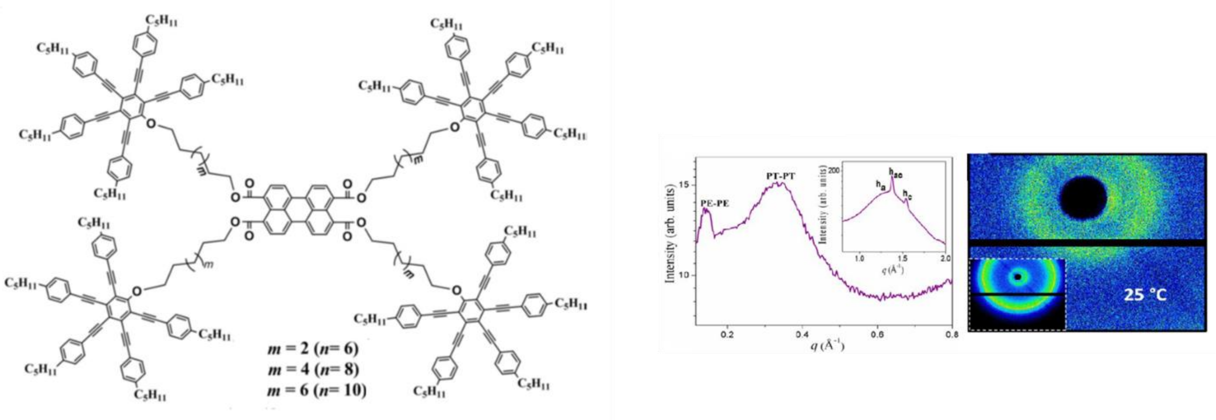


Figure 42. POM image, Diffraction pattern, and arrangement of N_{col} phase

d. Lateral Nematic (N_L): (**Figure 43**)

- Recently observed in shape amphiphilic systems (Mixing donor and acceptor of different shape resulting in charge-transfer complexes)
- Aggregation of disc-shaped molecules to form superstructures of discoidal morphology.
- Called lateral phase because of the presence of lateral interactions among the aggregates.
- Associated with high enthalpy changes for the phase transition and high relative correlation lengths in the parallel as well as in the perpendicular direction along the director.

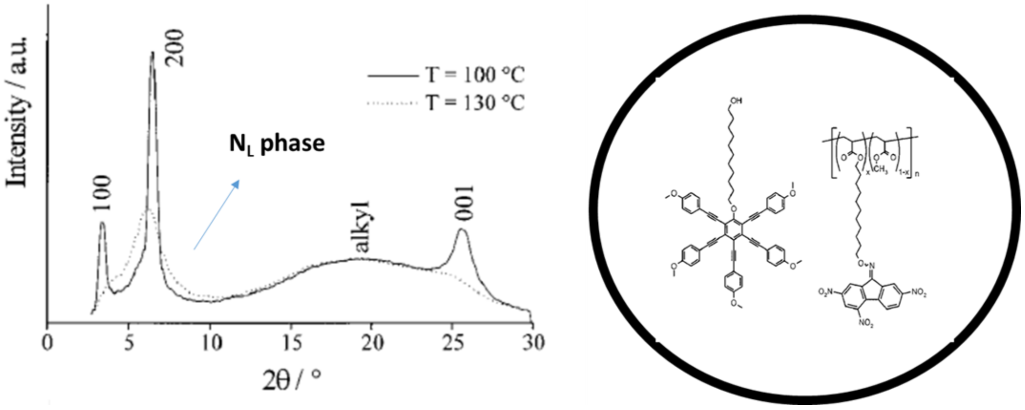


Figure 43. POM image, Diffraction pattern, and arrangement of N_L phase

Kouwer et al have done extensive studies on discotic nematogens and reported the following results. All four of them have identical symmetry so which leads to the appearance of schlieren texture under POM. It is very tedious to distinguish them using microscopy. But they can be distinguished from each other through diffraction data. Diffraction data gives an idea about the local order of all the above-mentioned phases (**Figure 44**). The extent of local order can be calculated by calculating the correlation length of a particular diffraction peak (can be obtained from the full width at half maximum of diffraction peak). From the correlation length (ξ), we can divide the corresponding d spacing (i.e either the small-angle reflection, fluidity peak of alkyl chains, core-core) which gives dimensionless quantity which is good yardstick to distinguish between them.

	Miller Index	N_D	N_{Col}	N_L
$(\xi/d)_{alkyl}$	***alkyl***	***2.3***	***2.3***	***2.3***
$(\xi/d)_{perpendicular}$	***200***	***2.0***	***2.8***	***8.5***
$(\xi/d)_{parallel}$	***001***	***4.2***	***8.5***	***8.5***

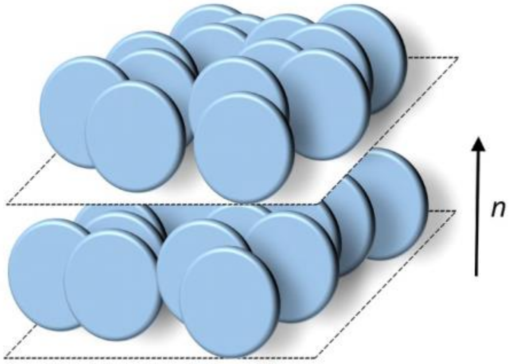
Figure 44. Characterizing N_D, N_{col}, $N_L$phase

Some of the general observations about nematic phases comprised of discotics are as follows

- Both N_{col} and N_L, generally found in charge transfer (CT) complexes so they often show deep colors under the microscope
- Viscosities of N_{col} and N_L are higher than normally observed for discotic nematic phase.
- Discotic nematic phase is least ordered, the N_D–I transition enthalpy is usually less than 1 kJ mol^{-1}.
- The isotropic transition enthalpies of N_{col} and N_L phases are 1–3 kJ mol−1 and about 5 kJ mol^{-1}, respectively.

1.4.5.3.3.2 Smectic phases of discotic mesogens:

The smectic organization in discotic results due to the uneven distribution of peripheral chains. The discs are arranged in a layered manner separated by a sublayer of peripheral chains. The possibility of biaxiality in these phases is quite bright due to the restriction of molecular rotation along the axes (**Figure 45**) . The smectic phases are quite rare in discotic systems.



$$1/d_l^2 = l^2/c^2$$

$$d_{001} : d_{002} : d_{003} : d_{004} ; \ldots. = 1 : 1/2 : 1/3 : 1/4 : \ldots.$$

Figure 45. Arrangement of Discotic lamellar phase

1.4.5.3.3.3 Columnar phases of discotic mesogens:

Since discotics liquid crystals are constituted by the π-fused central unit,they have strong π-π interactions among themselves. Due to strong π-π interaction, discotic molecules stack one on the top of the other that leads to formation of columns. These columns further self-organize themselves in various two-dimensional lattices. Within each column arrangement of molecules may be in a regular ordered (periodic) manner or disordered pattern (aperiodic). Periodic or aperiodic order of discs within the column is determined by the extent of π-π overlap along the column (**Figure 46**)

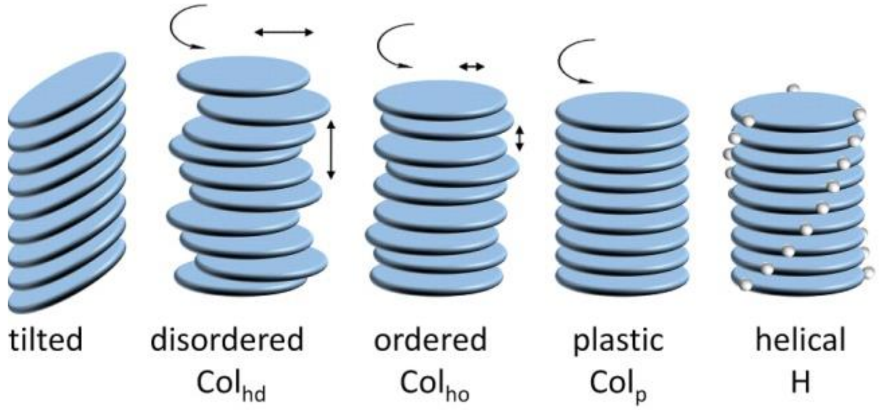


Figure 46. Types of Ordering of discs within columns

Depending on the degree of order in the molecular stacking (Figure 46), the orientation of the molecules along the columnar axis, the dynamics of the molecules within the columns and the two-dimensional lattice symmetry of the columnar packing, the columnar mesophases may be classified in seven classes (**Figure 47**)

1. Columnar hexagonal mesophase (Colh),
2. Columnar rectangular mesophase (Colr),
3. Columnar oblique phase (Colob),
4. Columnar plastic phase (Colp),
5. Columnar helical phase (H),
6. Columnar square (tetragonal) phase ($\mathrm{Col_{tet}}$), and
7. Columnar lamellar phase ($\mathrm{Col_L}$).

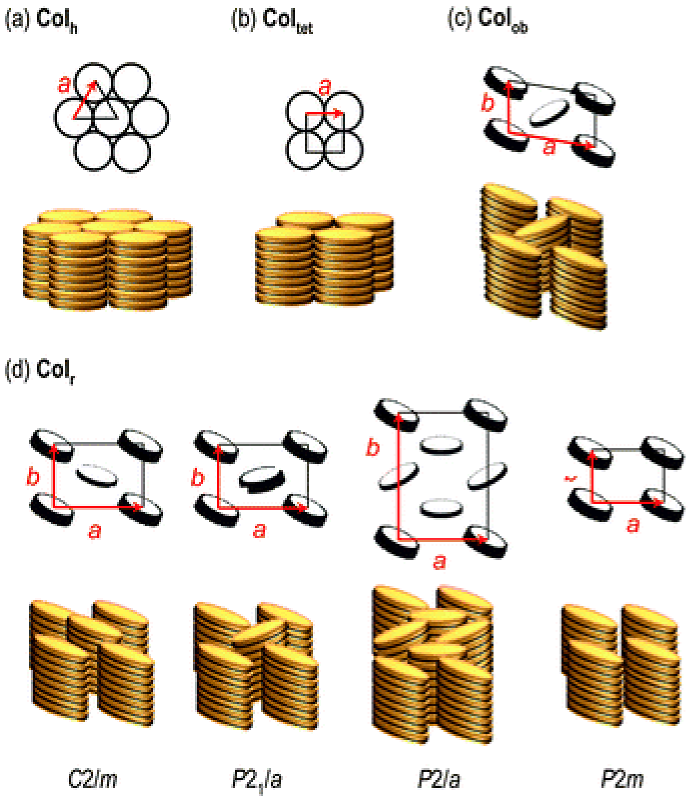


Figure 47. Different types of columnar phases

The types of columnar phases of discotic liquid crystalline systems are described in this section

Columnar hexagonal phase:

This is one of the prominently observed phases in the discotic compounds. They belong to space group P6mm. The typical X-ray diffraction pattern (XRD) of Col$_h$ shows diffraction rings in the small-angle region with their spacings are in the ratio of 1:1/√3:1/√4:1/√7: 1/√9. They show two broad peaks in the wide-angle range corresponding to fluid-like ordering of alkyl chains and core-core interactions due to the formation of columns. Under POM they often show spherulite, fan-shaped, and dendritic textures.

$$\frac{1}{d^2} = \left(\frac{4}{3}\right)\left(\frac{h^2 + hk + k^2}{a^2}\right)$$

$$1/d_{hk}^2 = 4/3((h^2 + hk + k^2))/a^2)$$
$$d_{100} : d_{110} : d_{200} : d_{210} : d_{300} : d_{220} : \ldots. = 1 : 1/\sqrt{3} : 1/2 : 1/\sqrt{7} : 1/3 : 1/\sqrt{12} : \ldots.$$

There are two types in this category ordered and disordered (**Figure 48**). The disc-shaped molecules are packed into columns by arranging in the orthogonal direction. Further, the arranged columns packs themselves into a two-dimensional hexagonal lattice. The stacking order with respect to intracolumnar stacking which differentiates between both with one having short correlation length(col$_{hd}$) (<10 molecules) and other having long correlation length (col$_{ho}$)(>>10 molecules) (**Figure 49**) . The appearance of the crystalline feature under POM is one of the notable points about this phase. Further, this crystalline-like appearance is justified by the fact the enthalpy values associated with Col$_{ho}$ to isotropic transition is high. Whereas the enthalpy of col$_{hd}$ to Isotropic transition is smaller as in the range of a typical LC to isotropic transition

Correlation length can be calculated by using the formula

$$\boldsymbol{\xi_s = \frac{0.89\lambda}{\beta\ cos\theta}}$$

β is full width at half maximum. The coefficient 0.89 is shape correction factor. (Depends on shape). In the case of regular ordered shapes β takes a value between 0.8 and 1. Both phases can be distinguishable by analyzing the correlation length associated with the core - core peak. Generally, col$_{ho}$ phase gives a sharp core - core peak, whereas col$_{hd}$ give a broader core core peak. The following example illustrates the above argument.

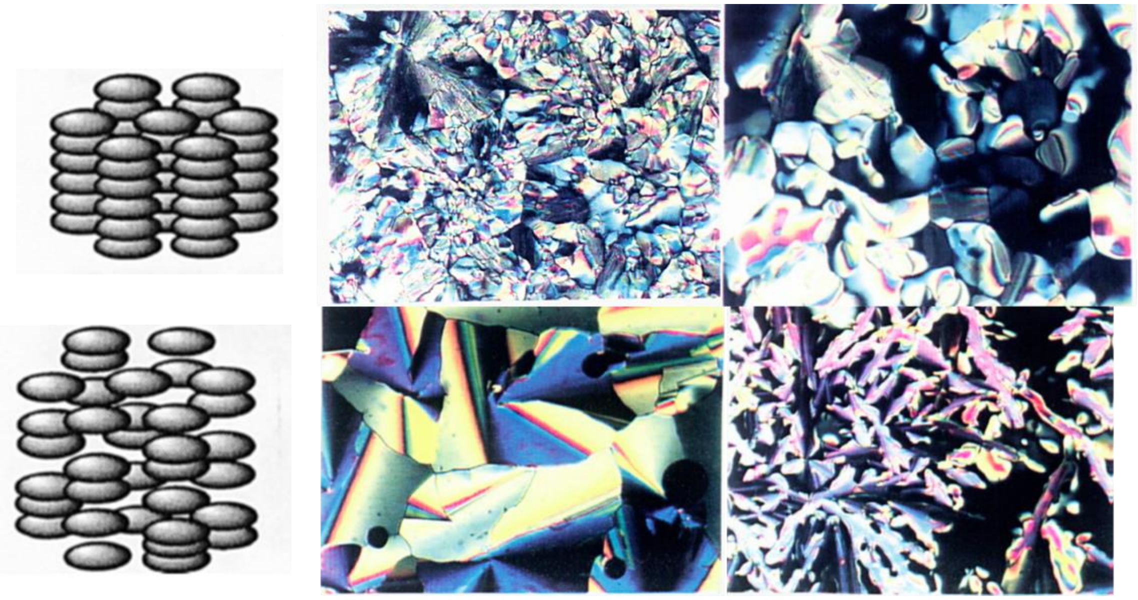


Figure 48. POM images and packing arrangement in ordered and disordered Col$_h$ phase

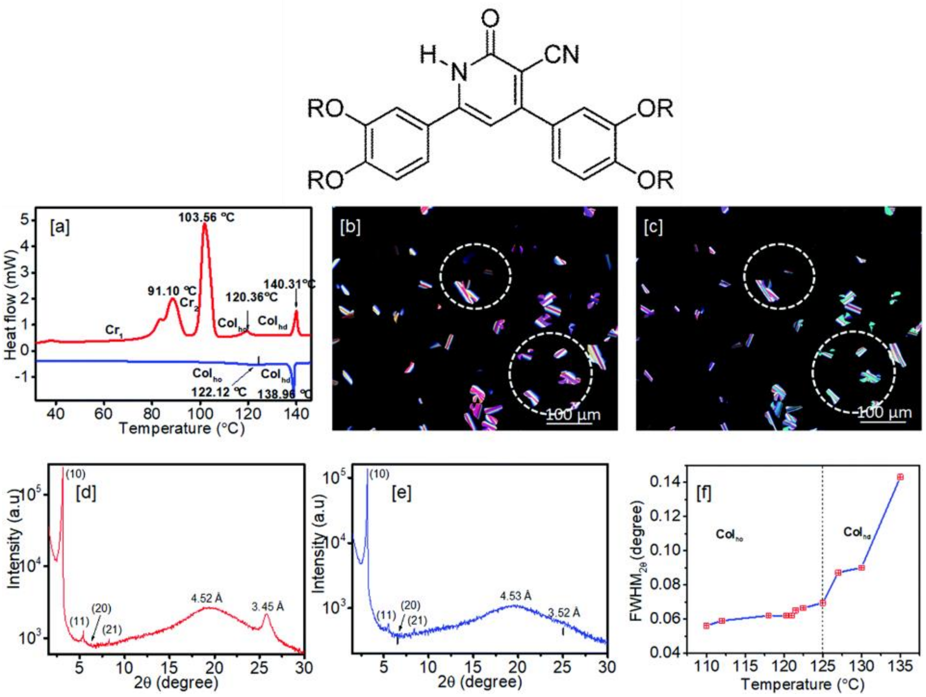


Figure 49. Distinguishing ordered and disordered col$_h$ phase[24]

Columnar rectangular phase:

Columnar rectangular phase has the main requirement of the tilted orientation of mesogens with respect to the stacking axis. They are more often found in systems with strong mesophases require a tilted orientation of the discotic molecules with regard to the columnar stacking axis and, consequently, are of higher order than Col$_h$ mesophases. They are often observed in mesogens with strong π-π interactions. All the rectangular phases are reported to be biaxial in nature. (One axis is parallel to column axis, other is parallel to molecular axes). Stronger core-core interactions are needed for the formation of the rectangular phases because of the tilted nature of columns, In the same series on increasing side chain length, crossover from columnar rectangular to hexagonal mesophases phase transition have been reported.

Col$_r$ mesophases are divided into three different planar space groups: P21/a, P2/a, or C2/m based on crystallographic conditions (**Figure 51**). In X-ray diffraction patterns, two strong reflections (due to the splitting of the (10) reflection of the hexagonal lattice) in the small-angle region are the signature reflections of Col$_r$ phases. The enthalpy involving the rectangular phase to the hexagonal phase is very small as the transition falls under the second-order phase transition. Because there is only change in the tilting of the molecules in the columns. Most commonly observed pattern of the texture of the Col$_r$ mesophase is broken fan-shaped (**Figure 50**).

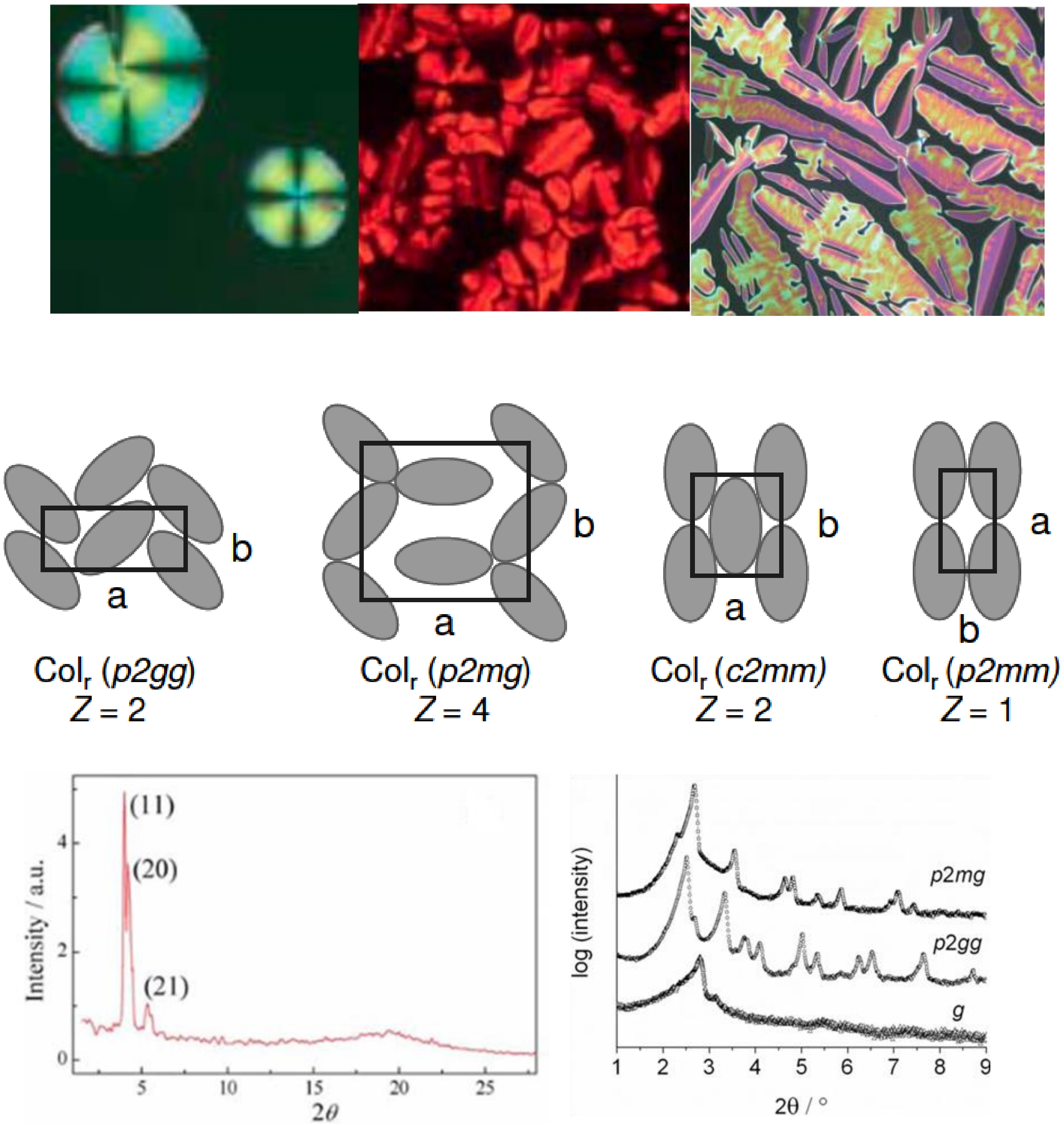
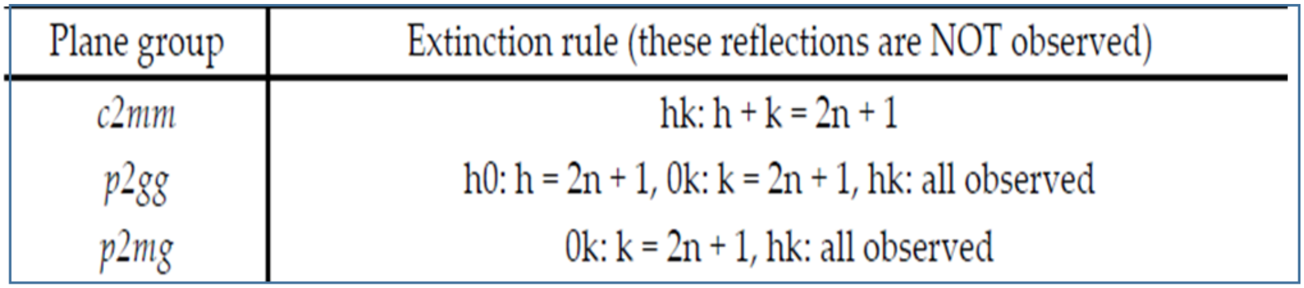


Figure 50. POM images and diffraction patterns of Col$_r$ phase[25]



Plane group	Extinction rule (these reflections are NOT observed)
c2mm	hk: h + k = 2n + 1
p2gg	h0: h = 2n + 1, 0k: k = 2n + 1, hk: all observed
p2mg	0k: k = 2n + 1, hk: all observed

Figure 51. Distinguishing between three Col$_r$ phases

Columnar tetragonal phase:

This phase is also called a columnar square phase. Here the columns are upright and they are arranged in a square lattice. These phases often tend to exhibit spontaneous homeotropic alignment of the columns like hexagonal counterparts. POM images show dendritic type textures (**Figure 52**).Generally, this mesophase is exhibited by sugar molecules, phthalocyanines and supramolecular fluorinated liquid crystals. The small-angle spacings will be in ratio 1:1/√2: 1/2 and so on.

$$1/d_{hk}^2 = (h^2 + k^2)/a^2$$

$$d_{100} : d_{110} : d_{200} : d_{210} : d_{220} : d_{300} : \ldots = 1 : 1/\sqrt{2} : 1/2 : 1/\sqrt{5} : 1/\sqrt{8} : 1/3 : \ldots$$

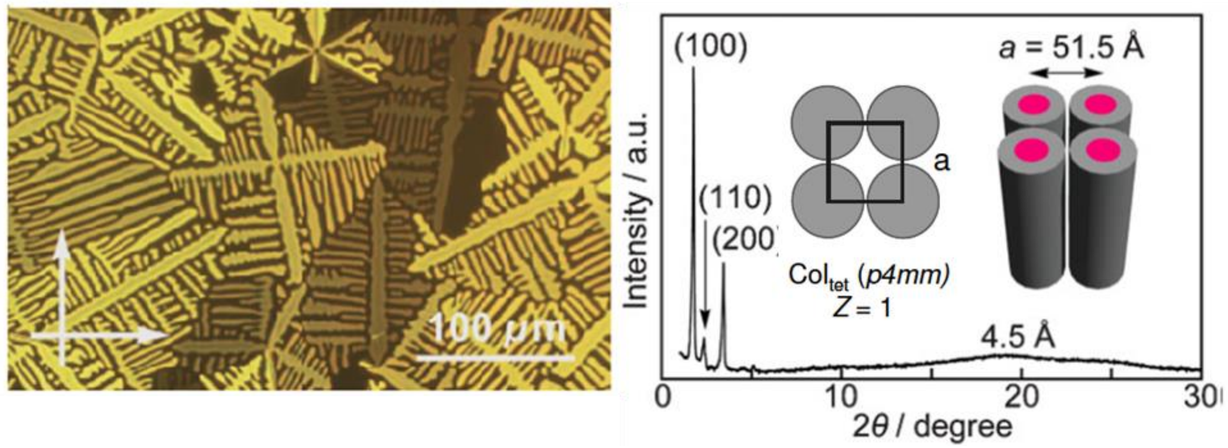


Figure 52. POM images and diffraction patterns of Col$_{sq}$ (tetragonal) phase

Columnar Oblique phase (Col_{ob}):

The arrangement of molecule in this phase is very similar to that of rectangular but the columns are arranged askew to one another. This phase is very rarely observed in discotics. They belong to space group P1**. (Figure 53)**

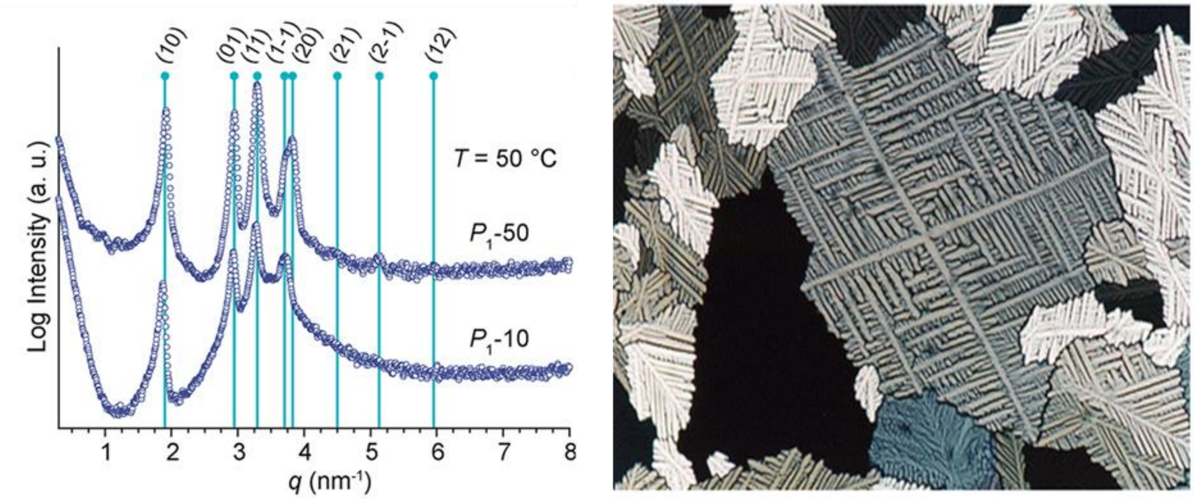


Figure 53. POM images and diffraction patterns of columnar oblique phase

Columnar plastic phase (col_{hp} or col_{rp}):

The plastic phase is characterized by three-dimensional crystal-like order but the columns are arranged in 2-dimensional hexagonal lattices. The disks within the columns have the freedom to rotate along the columnar axis. The diffraction pattern shows small-angle peaks that can be indexed into a hexagonal or rectangular or oblique lattice (recently reported), In the wide-angle region, around 3.4 Å they show two sharp reflections which are considered to be a typical signature for a plastic phase. The plastic phase is differentiated from crystal by the presence of fluidity peak of alkyl chains. One of the widely studied compounds Hexabutyloxy triphenylene (H4TP) and its derivatives were reported for their plastic nature of mesophase. The correlation length variation between plastic phases to the hexagonal phase is shown in the **figure 54**.

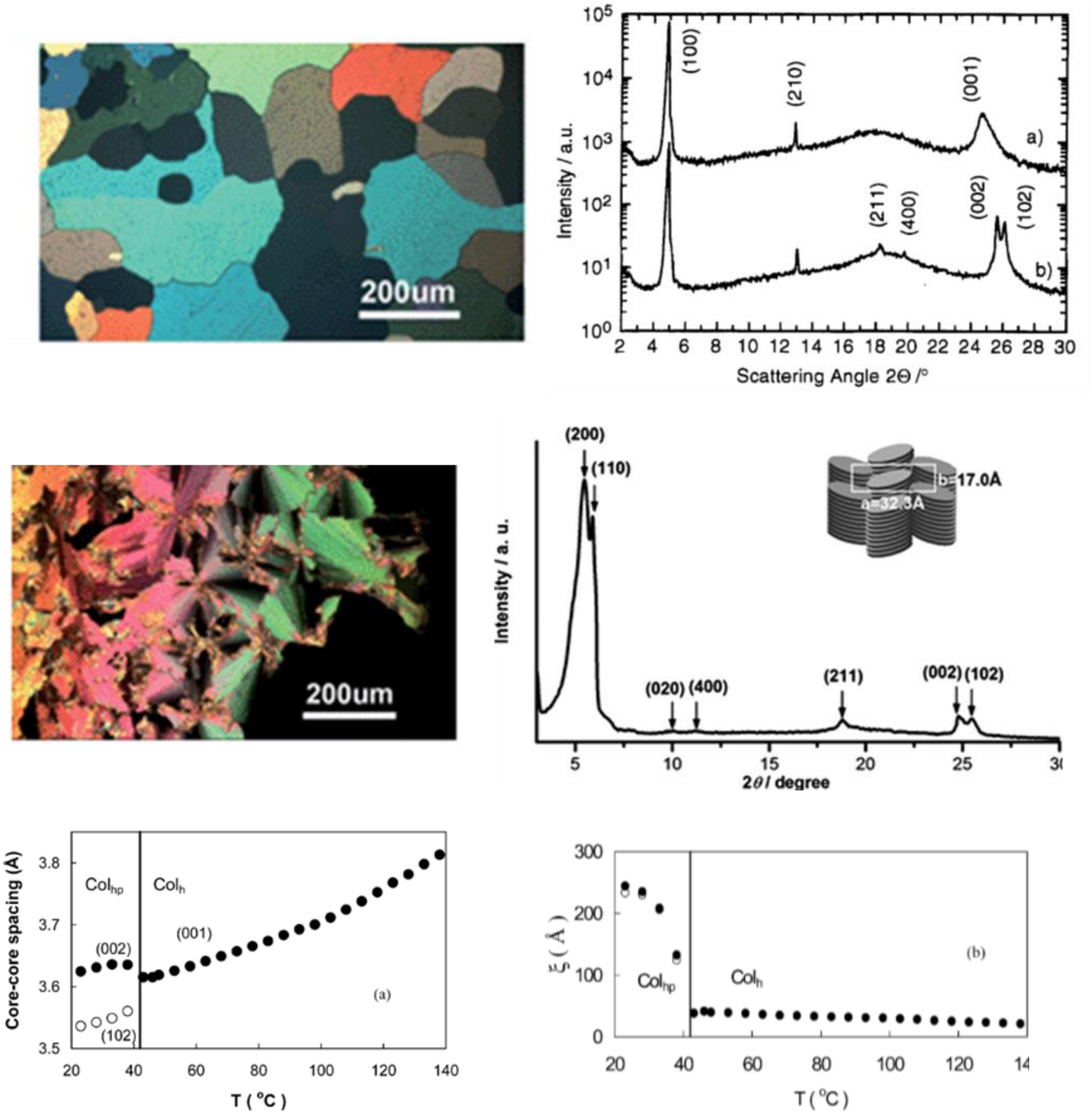


Figure 54. POM images and diffraction patterns of columnar plastic phases

Columnar helical phase:

The arrangement involves the helicoidal stacking of cores. Further within columns, the intermolecular spacing is out of proportion compared to the helical period. Generally, they form a superlattice containing three columns because of molecular interdigitation in a triangular structure. In the superlattice, the third columns are positioned exactly half an intercolumnar distance vertically with respect to other columns. The typical diffractogram is shown in figure. They are chiral in nature even when they do not have any chiral influence due to chiral centers.

In the diffraction pattern, they give rise to two sets of peaks. One is corresponding to a hexagonal lattice. Other sets of peaks confirm the helical nature in the arrangement (**Figure 55**).

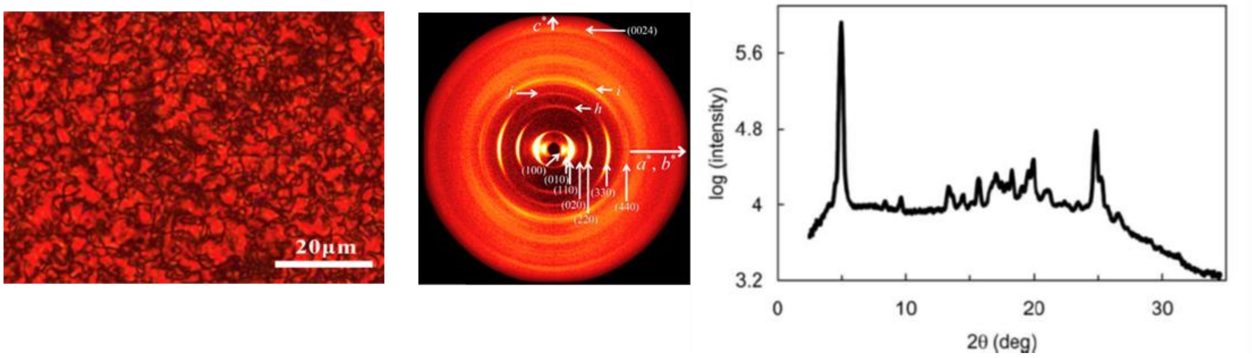
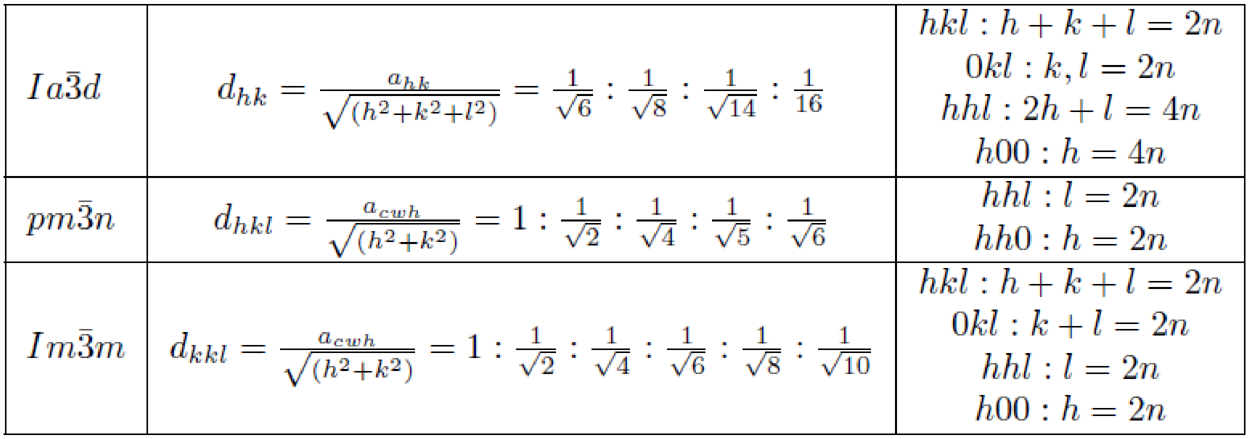


Figure 55. POM images and diffraction patterns of columnar helical phase

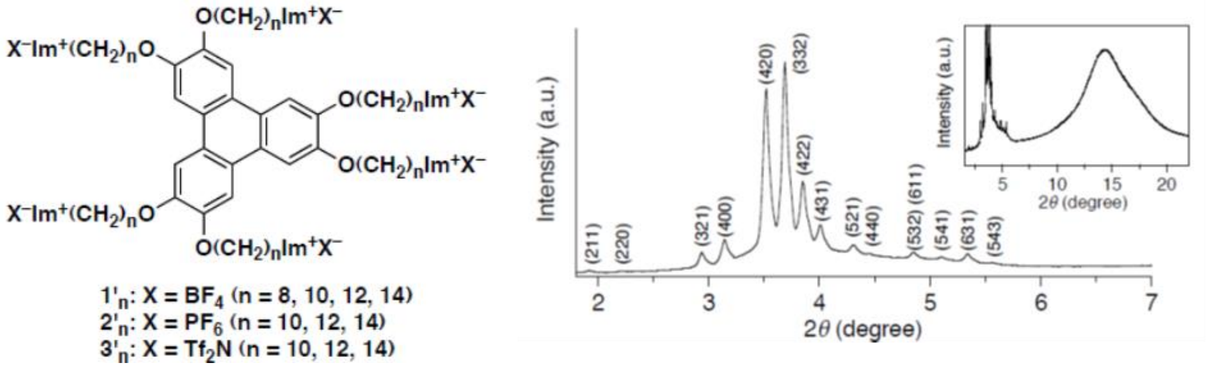
Cubic columnar phases:

Cubic phases are prominently observed in lyotropic systems. There are reports of cubic arrangement in discotic compounds involving phthalocyanines and triphenylene. Generally, they give rise to bicontinuous phases. They will look very viscous to the naked eye. These phases are optically isotropic. The only way to confirm this phase is through diffraction (**Figure 57**). The cubic phases can be of three types based on space-group symmetry. The ratio of d spacings and their extinction rules are given below (**Figure 56**)



$Ia\bar{3}d$	$d_{hk} = \frac{a_{hk}}{\sqrt{(h^2+k^2+l^2)}} = \frac{1}{\sqrt{6}} : \frac{1}{\sqrt{8}} : \frac{1}{\sqrt{14}} : \frac{1}{16}$	$hkl : h+k+l = 2n$ $0kl : k, l = 2n$ $hhl : 2h+l = 4n$ $h00 : h = 4n$
$pm\bar{3}n$	$d_{hkl} = \frac{a_{cwh}}{\sqrt{(h^2+k^2)}} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{5}} : \frac{1}{\sqrt{6}}$	$hhl : l = 2n$ $hh0 : h = 2n$
$Im\bar{3}m$	$d_{kkl} = \frac{a_{cwh}}{\sqrt{(h^2+k^2)}} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{6}} : \frac{1}{\sqrt{8}} : \frac{1}{\sqrt{10}}$	$hkl : h+k+l = 2n$ $0kl : k+l = 2n$ $hhl : l = 2n$ $h00 : h = 2n$

Figure 56. Extinction rules for cubic phases of different space groups



$1'_n$: X = BF_4 (n = 8, 10, 12, 14)
$2'_n$: X = PF_6 (n = 10, 12, 14)
$3'_n$: X = Tf_2N (n = 10, 12, 14)

Figure 57. POM images and diffraction patterns of cubic phase

Columnar Lamellar phase:

Certain discotic compounds were found to show smectic mesophases. Example: some phthalocyanines and perylenes derivatives. This mesophase was denoted by col $_L$. The molecular arrangement associated with this phase is as follows, the columns formed by a stack of molecules arranged in layers. Further, the columns constituting the same layer can have sliding movement whereas the columns in different layers lack translational correlation between them. The diffractograms give typical smectic like pattern. The peaks in small-angle will have their spacings in their ratio 1:2:3. The wide-angle gives rise to peak corresponding to distance of intracolumnar separation validates the layer like arrangement of columns (**Figure 58**).

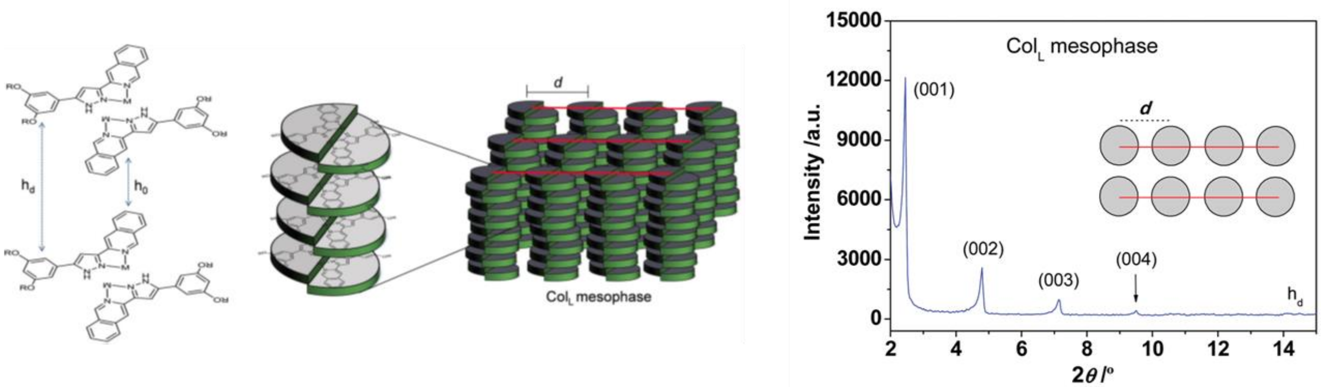


Figure 58. POM images and diffraction patterns of Col $_L$ phase

1.5 Lyotropic liquid crystals:[26]

Lyotropic liquid crystals were known since Bronze Age as they form the basis for the soap making process. In 1850, their texture was observed in a mixture comprised of phospholipid myelin and water. Lyotropic liquid crystalline systems have a great scope in the detergent and cosmetic industry. Lyotropic liquid crystals are always shown in mixtures as the material is dispersed in a solvent continuum. The solvent generally used is water. Some non-aqueous solvents (includes ionic liquids, organic solvents, inorganic salts) also were used as medium for dispersing the material. The driving forces for the formation of liquid crystalline phases of these amphiphilic molecules are the micro-segregation of hydrophilic and hydrophobic molecular parts into different regions (interface curvature), as well as the strong attractive forces between the hydrophilic head groups, such as intermolecular hydrogen bonding.

The amphiphilic substance which is dispersed in the solvent continuum constitutes the other component. The main requisite of the material to form the lyotropic phases in a given medium is that the substance should be amphiphilic in nature. The amphiphilic materials are those materials that have two parts in their structures one is the lyophilic (solvent loving) other one is lyophobic (solvent-hating). The differential interaction of different parts in the same compounds with the medium results in the formation of mesophases. When an amphiphile for example surfactant is taken in an aqueous medium, they show slight solubility behavior at low concentrations. This minimal solubility induces the random distribution of amphiphiles throughout the medium which suggests that they lack order. But on increasing the amount of amphiphile i.e concentrations above the threshold limit called critical micelle concentration (CMC)

Water miscible surfactants are dissolved in very low concentration, the molecules are distributed randomly throughout the water without any order. However, upon increasing the concentration above a well-defined limit known as the critical micelle concentration (CMC), they form aggregate structures which are called micelles (**Figure 59**). Micelles can be of two types

1. The normal micelle (oil in water) where hydrophobic part (the tail) lies inside the micelle core and hydrophilic part (head group) exposed to the aqueous medium.
2. Inverse micelles generally formed in non-polar solvents (water in oil)where solvophobic head groups lies at the center and solvophilic tails protruding out towards the solvent

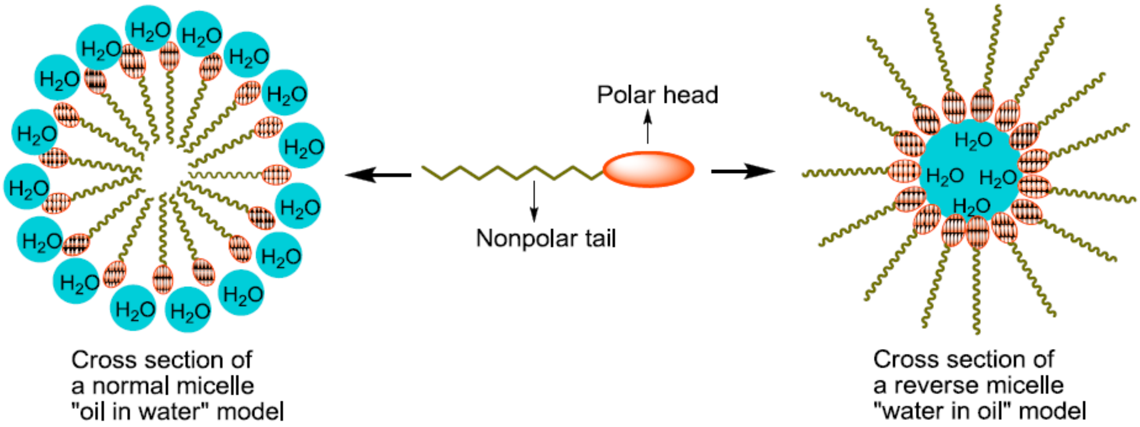


Figure 59. Formation of micelles

1.5.1 Constituents of lyotropic liquid crystals:

The lyotropic liquid crystals are usually formed using water and one or two surfactants and possibly oils within a definite concentration and temperature range. In the lyotropic systems, solvent molecules occupy the space around the amphiphilic compounds which gives fluidity to the whole system. On comparing with thermotropic liquid crystals, these lyotropic have another parameter i.e the concentration which plays a vital role in the induction of different phases. The interaction of amphiphiles with solvent is the main reason for the formation of these self-assembled structures. The amphiphile can be of ionic, nonionic or zwitterionic in nature.

1.5.2 Formation of micelles.

When a surfactant is introduced into the solvent medium, at lower concentrations they dissolved in the medium at lower compositions. As the composition of amphiphile increases, they achieve a critical limit where they tend to aggregate into micelles which are called as an isotropic micellar solution. Micelles generally consist of 20-100 surfactant molecules and their characteristic size is 10-20 nm. The micelles are dynamic in nature. Because of the presence of the hydrocarbon chains of surfactant molecules which are known for their conformational flexibility (the average life-time 10^{-10} s. Water and surfactant molecules undergo a fast rotational and translational diffusion which takes 10^{-12} s. A surfactant monomer stays 10^{-6} – 10^{-3} s in a micelle before either dissolution in the solvent or formation of aggregates and the life-time of a micelle is between 10^{-2} to 10 s.

The limiting solubility of surfactant molecules in the solvents is called as critical micelle concentration. An amphiphile when the concentration is below CMC, they are present in monomeric form. When the concentration crosses CMC, they adopt aggregate structures. This monomer to aggregate transition can be thought of as analogous to the phase transition of vapor state to condensed phase.

Formation of micelles by an amphiphile depends on two factors

1. Hydrophobic effect: induces the segregation of nonpolar part from the water
2. Interactions among the polar head groups: determines the extent of close packing of aggregated structures

1.5.3 Thermodynamics of Micelle formation:

The process of micelle formation is associated with loss of entropy as the free monomers assembled into ordered aggregates. Even though micellization is associated with loss of entropy, it is a spontaneous process. The spontaneity of Micellization can be explained as follows. Micelle formation involves both surfactant and water. When a hydrophobic substance is introduced into water there will be a cavity created in the water phase which accommodates the surfactant. But the tendency of water molecules in involving in hydrogen bonding among themselves induces them to from ordered structure around the surfactant chains. Transfer of hydrocarbon chains from water medium to micellar aggregates dissipates the cavity which leads to the availability of more microstates for the bulk water. This process gives the entropic requirement for micellization. The process where the spontaneous formation of micelles is induced by the increase in entropy when water molecules around the nonpolar part of the surfactant is released as the nonpolar part assembles into a micellar structure is called the hydrophobic effect.

1.5.4 Role of the molecular geometry[27]

When surfactant concentrations crosses above the CMC, micelles in solution will begin to pack together in ways that depend on the geometry of the individual micelles. The molecular structure of surfactants plays a major role in the determination of morphology of aggregates. The structures are sensitive to concentration, pH and other thermodynamic parameters.

The basic theory of micellization was constructed and described qualitatively by Mitchell, Niham, Israelachvili. The theory states as follows,” The aggregates formation by surfactants is controlled by molecular geometry. The geometric approach used the following three parameters

a. Minimum Interfacial area occupied by head group(a_o) (**Figure 60**)
b. The volume of hydrophobic tails (V)
c. Maximum Extended chain length of tails in the micellar core (l_c)

$$\mathbf{P_c = v/\,(a_0 l_c)}$$

. The possible aggregation characteristics of surfactants cover a wide range of geometric arrangement,are given in Figure 60.

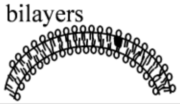
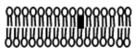
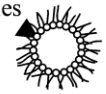
Critical packing parameter $P_c=v/a_0l_c$	Critical packing shape	Structures formed
$P_c<1/3$	Cone 	Spherical micelles 
$1/3<P_c<1/2$	Truncated cone 	Cylindrical micelles 
$1/2<P_c<1$	Truncated cone 	Flexible bilayers 
$P_c\cong1$	Cylinder 	Planar bilayers 
$1<P_c$	Negative curvature 	Oil soluble micelles 

Figure 60. Critical packing parameter for various different micelles

1.5.5 Lyotropic liquid crystalline structures[28]

The micellar aggregates can assemble into following liquid crystalline structures as determined by parameter p_c.

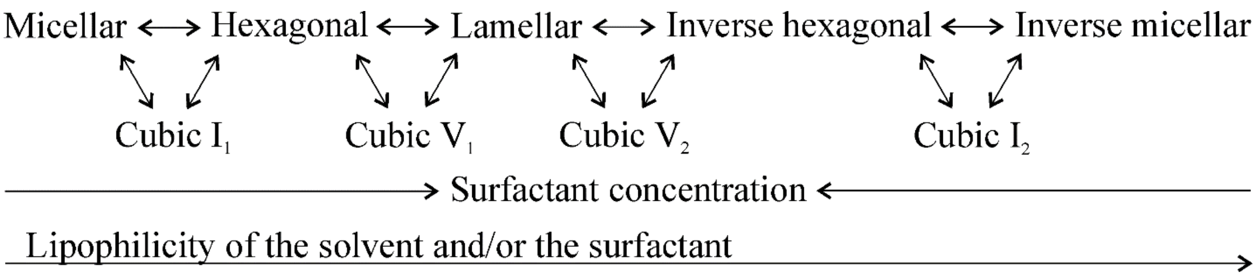
Normal (Type 1) self-assembled structures, with positive curvature towards the water, are formed when *v/al* < 1,

Inverse structures (Type 2) exhibit negative curvature away from water, *v/al* > 1.

At the point i.e. v/al =1 lamellar bilayer structures are observed.

The characterization of all these lyotropic structures can be done via microscopy and diffraction experiments. The diffraction parameters of these phases are given in the table below. Mesophase identification is done based on viscosity and observation of the characteristic birefringent textures that can be seen when viewed under crossed polarised light.

The typical phase transition observed as a function of surfactant concentration is given in the following schematic (**Figure 61**) (**Figure 62**)



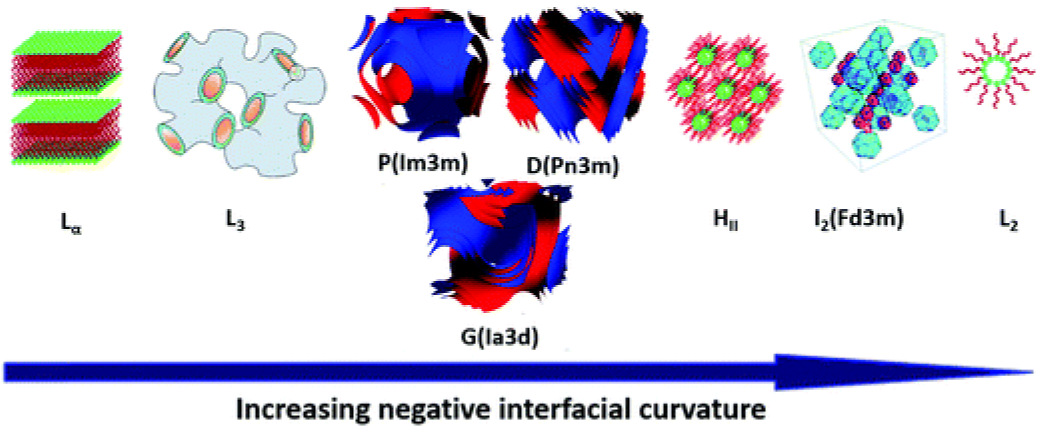


Figure 61. Different lyotropic phases

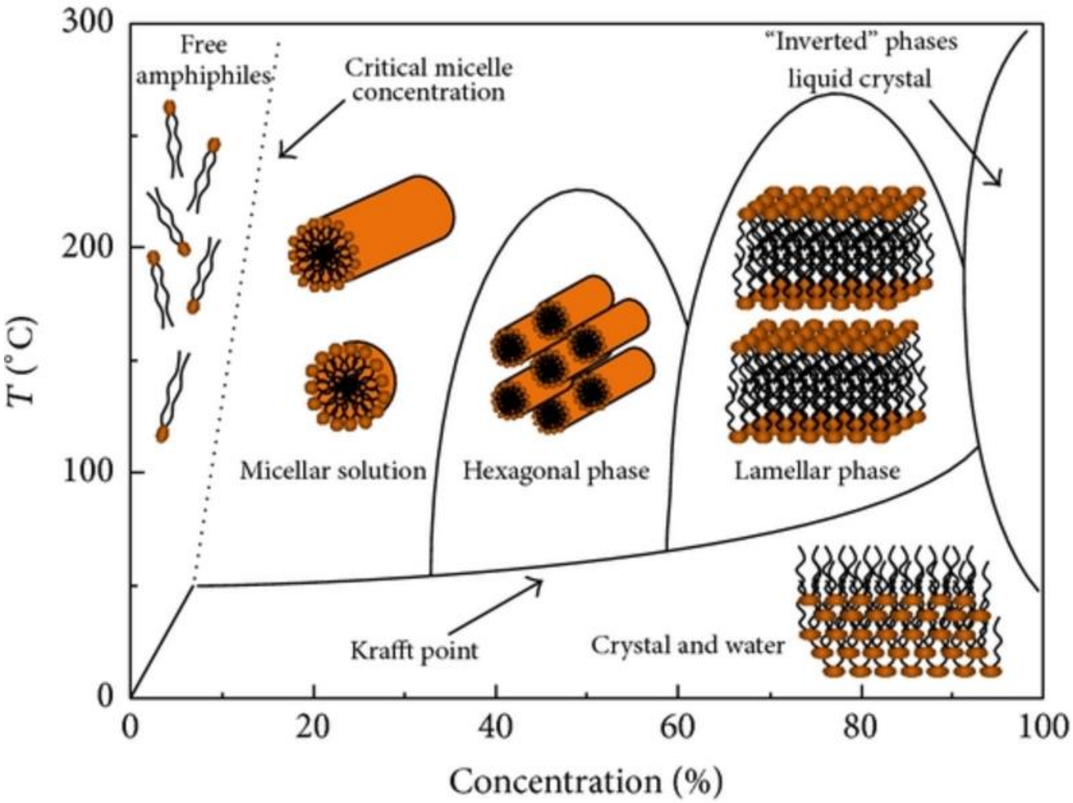


Figure 62. Amphiphile-water phase diagram

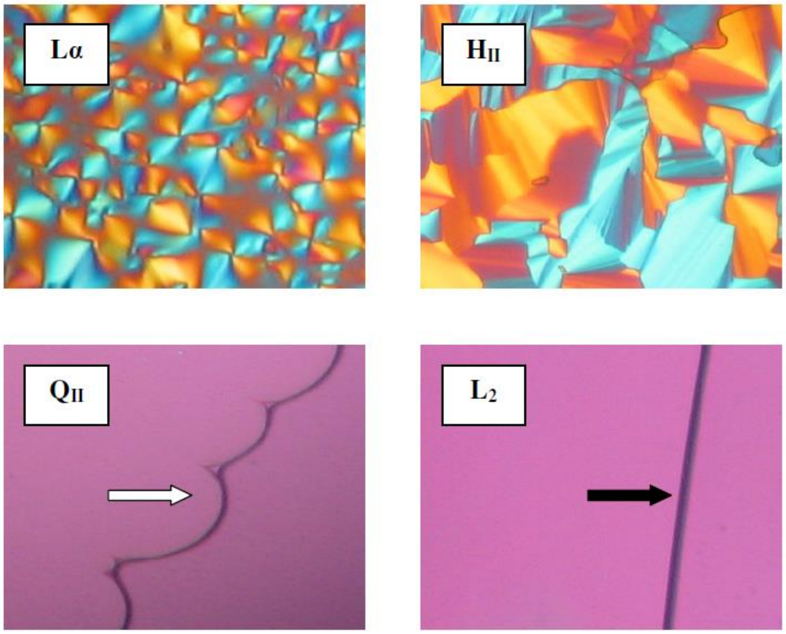
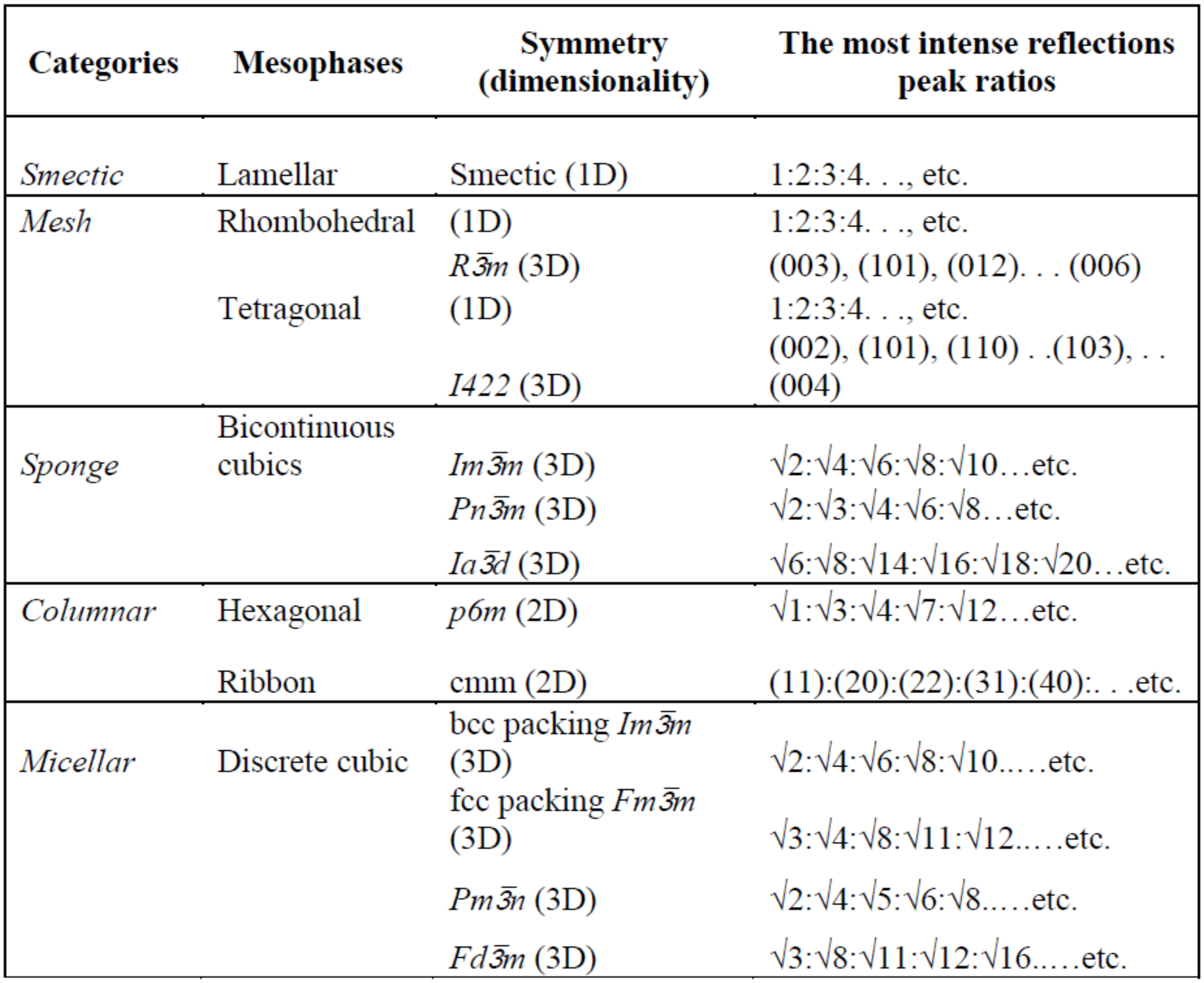


Figure 63. POM images of different lyotropic phases



Categories	Mesophases	Symmetry (dimensionality)	The most intense reflections peak ratios
Smectic	Lamellar	Smectic (1D)	1:2:3:4. . ., etc.
Mesh	Rhombohedral	(1D)	1:2:3:4. . ., etc.
		$R\bar{3}m$ (3D)	(003), (101), (012). . . (006)
	Tetragonal	(1D)	1:2:3:4. . ., etc.
		$I422$ (3D)	(002), (101), (110) . .(103), . . (004)
Sponge	Bicontinuous cubics	$Im\bar{3}m$ (3D)	√2:√4:√6:√8:√10…etc.
		$Pn\bar{3}m$ (3D)	√2:√3:√4:√6:√8…etc.
		$Ia\bar{3}d$ (3D)	√6:√8:√14:√16:√18:√20…etc.
Columnar	Hexagonal	$p6m$ (2D)	√1:√3:√4:√7:√12…etc.
	Ribbon	cmm (2D)	(11):(20):(22):(31):(40):. . .etc.
Micellar	Discrete cubic	bcc packing $Im\bar{3}m$ (3D)	√2:√4:√6:√8:√10..…etc.
		fcc packing $Fm\bar{3}m$ (3D)	√3:√4:√8:√11:√12..…etc.
		$Pm\bar{3}n$ (3D)	√2:√4:√5:√6:√8..…etc.
		$Fd\bar{3}m$ (3D)	√3:√8:√11:√12:√16..…etc.

Figure 64. X-Ray diffraction details for various lyotropic phases

1.5.6 Biological liquid crystals:

Lyotropic liquid crystals are more often found in biological systems. Biological molecules have a tendency to aggregates themselves in presence of solvent (i.e water)[29]. The reports on lyotropic liquid crystalline systems based on biological materials has found his importance in various applications such as tissue engineering. Liquid crystalline phases have been identified in many structural and functional biological materials, here we summarize examples ranging from phospholipid cell membranes to some concentrated DNA and protein solutions in the secretion of spiders used to generate silk (**Figure 65**). The importance of LC organization in biological systems have the following notable features such as follows

a. Efficient packing (eg. DNA)
b. Surface directed self-organization (eg, Cellulose)
c. Low viscosity (silk)
d. Sensing actuators (hair cells)[30]
e. Mechanical strength (chitin, cellulose)

The mesophase often found in biological systems are usually cholesteric in nature.

BIOPOLYMER	FUNCTION	LC ORGANISATION	OCCURRENCE
DNA			
Chromosomal DNA	Efficient packing	Cholesteric	*In vivo*
Phage DNA	Efficient packing	Columnar	*In vivo*
Bacterial Plasmids	Efficient packing	Cholesteric	*In vivo / In vitro*
Glycopolymers			
Cellulose	Structural	Helicoidal / Cholesteric	*In vitro / In vivo*
Starch	Reservoir of energy	Smectic	*In vitro*
Chitin	Structural	Helicoidal / Cholesteric	*In vitro / In vivo*
Lipids			
Phospholipids	Structural/Functional	Layered lamellar	*In vivo / In vitro*
Proteins			
Collagen	Structural	Nematic / Cholesteric	*In vivo / In vitro*
Spider Silk	Structural / Functional	Nematic	*In vivo / In vitro*
Silkworm Silk	Structural / Functional	Nematic	*In vivo / In vitro*
F-actin	Structural / Functional	Nematic / Smectic	*In vitro*
Microtubules	Structural / Functional	Nematic	*In vitro*
β-Lactoglobulin	Functional	Nematic	*In vitro*
Lisozyme	Functional	Nematic	*In vitro*
Insulin	Functional	Nematic	*In vitro*

Figure 65. Examples of biological liquid crystals[31]

1.5.7 Chromonics

Chromonic Phases:

Lyotropic chromonic liquid crystals (LCLCs) were first observed by Sandquist in 1915[32]. They have shown great potential but still, they have been poorly understood in terms of their formation Most of the reported molecules belong to the class of dyes, drugs, nucleic acids, and some nonionic discotic amphiphiles. The name chromonic was originated from an anti-asthmatic drug called DSCG (disodium cromoglycate) because this is one of the widely studied compounds for its chromonic mesomorphism. [33]

Important aspects of chromonic phases:

Chromonic mesophases are lyotropic isotopes of the discotic mesophases. The requirement for a chromonic mesogen involves a disk-like core with hydrophilic groups in the periphery (can be of ionic, H-bonding with solvent in nature). In the solvent, they often show a tendency to aggregate. The aggregate formation is mainly induced by π-π interaction between the aromatic cores. The figure shows examples of compounds reported for their chromonic behavior. (**Figure 66**)

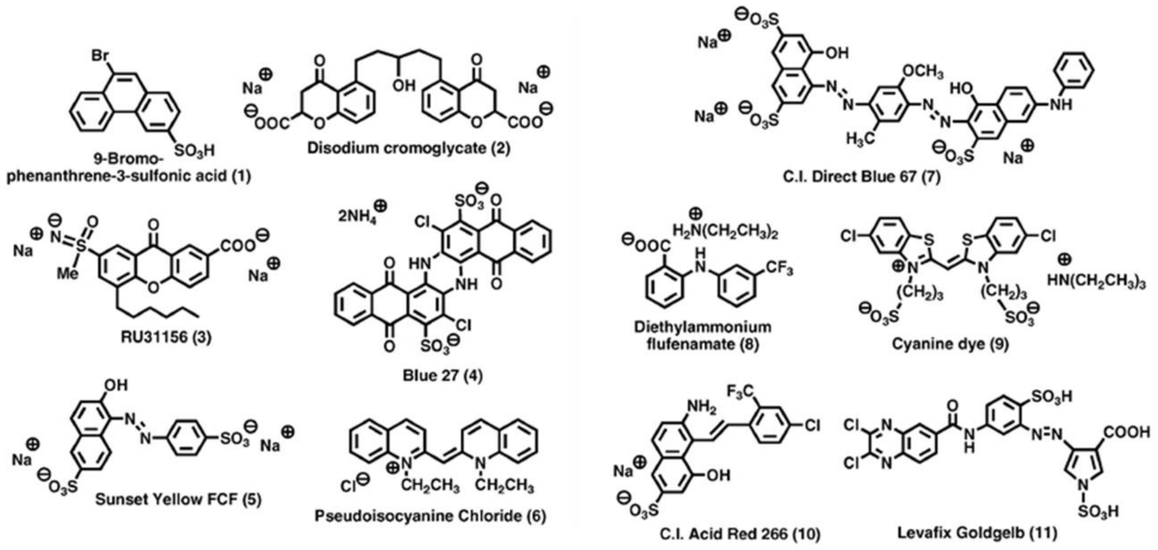


Figure 66. Examples of Reported Chromonic Mesogens

The chromonic systems stack into columns in order to avoid the interaction of hydrophobic rings with aqueous or any hydrophilic solvent. The stacking process is observed even in a low concentration regime. On increasing the concentration of dye molecule, the column length was fund to grow further and at the same time, the amount of hydrophilic surface exposed to the solvent continuum also decreases without reaching minimum free energy state. This kind of aggregation behavior is termed as isodesmic assembly[34]. Isodesmic assembly can be defined as when you add or remove one molecule from a stack which always gives the same change of Gibbs free energy independent of the length of the column (**Figure 67**). Other notable aspect of chromonic phases are as follow, in typical surfactants, at a lower temperature, the flexible alkyl tails usually dynamic in their hydrophobic region freezes out to lead to gel phase. This hampers the formation of micelle. The threshold temperature limit is called Kraft temperature. In the case of chromonics, because of the absence of alkyl chains, there is no such observation. They usually don't show the kraft point. The phases they usually exhibit are chromonic N (nematic) and chromonic M (hexagonal) (**Figure 68-73**)

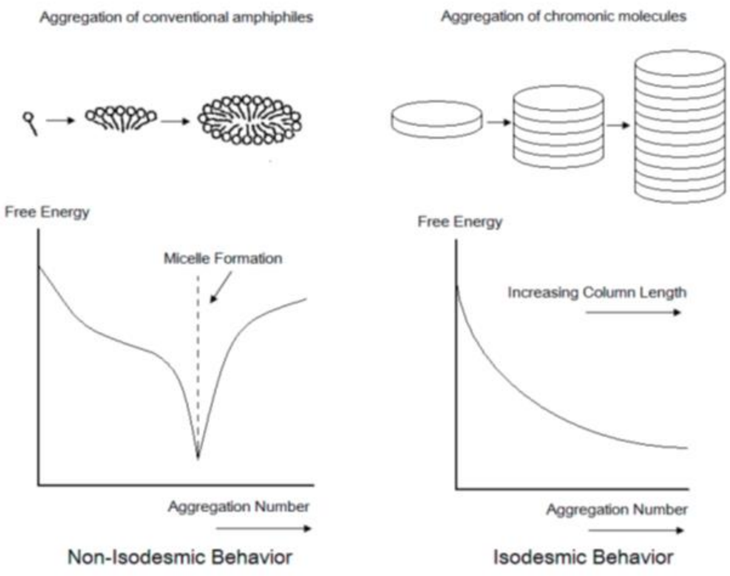


Figure 67. Isodesmic Assembly

Difference between chromonics and other lyotropic phases[35]:

Property	Amphiphilic mesophases	Chromonic mesophases	Polymeric mesophases
Molecular Structure	Molecules with hydrophilic and hydrophobic parts	Planar polyaromatic molecules with hydrophilic units	Linear rigid polymers
Examples	Soaps, detergents	Drugs, Dyes	Biological or synthetic polymers
Surface properties	Highly surface-active	No surface activity	Can be surface active
Types of aggregation	Micellar aggregates results above a threshold concentration guided by the hydrophobic effect.	No threshold concentration. Very gradual aggregation as a function of concentration at low concentration regime	None
Thermal behaviour	Shows Kraft temperature	No Kraft temperature	No Kraft temperature
Mesophases involved	Cubic, Hexagonal lamellar, inverse phases, Nematic	Nematic and Hexagonal	Nematic and many phases
Diffraction pattern	Characterstic broad reflection around 4.5Å due to aggregation of alkyl tails	Characterstic stron sharp reflection around 3.4Å due to stacking of aromatic rings	Hexagonal packing for large rod like polymers

Figure 68. Chromonic VS other lyotropic systems

TYPES OF CHROMONIC PHASES

Phase	Description
Chromonic N	**The columns in N are more or less parallel, but there is no positional order ordering with only orientational long-range order of stacking columns**
Chromonic M	**The M phase has an array of parallel columns with orientational and positional long-range order of column long axes. The columns are stacking on a lattice with statistical hexagonal symmetry.**
Chromonic P	**An array of parallel columns lying on hexagonal symmetry with positional and orientational long-range order of column long axes.**
Chromonic O	**The O phase has parallel columns lying on a rectangular lattice with orientational and positional long-range order of columns long axes**

Figure 69. Overview Of types of chromonic mesophases

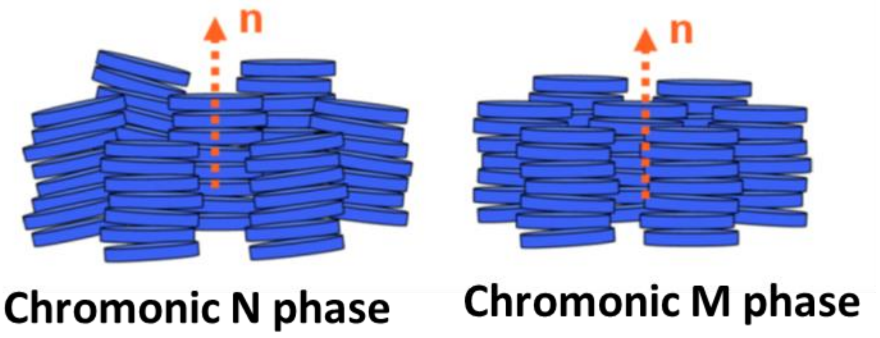


Figure 70. Schematic of Chromonic N phase & Chromonic M phase

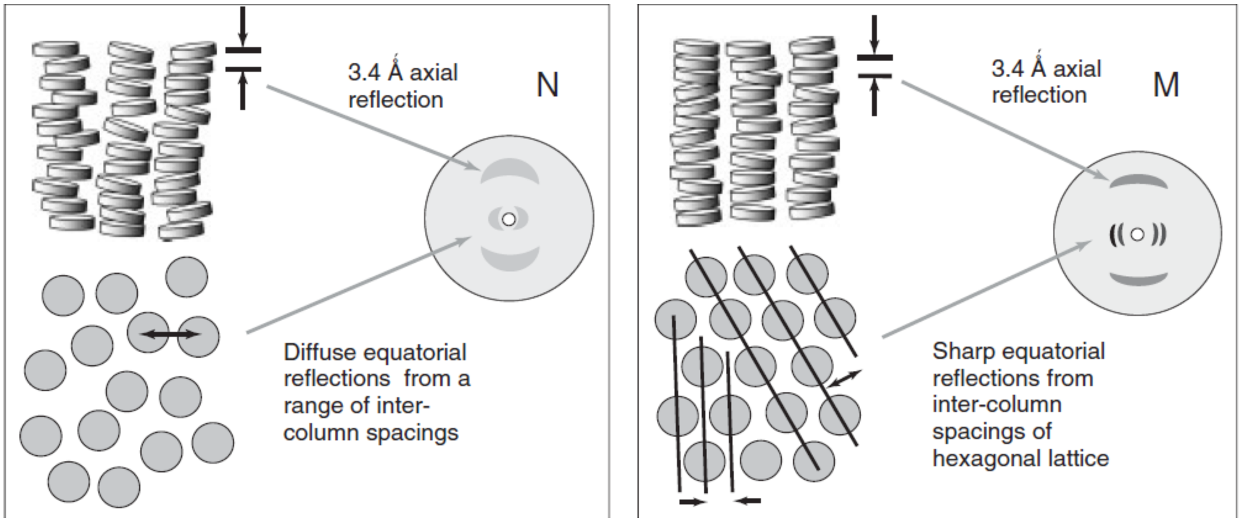


Figure 71. Diffraction pattern of Chromonic N phase & Chromonic M phase

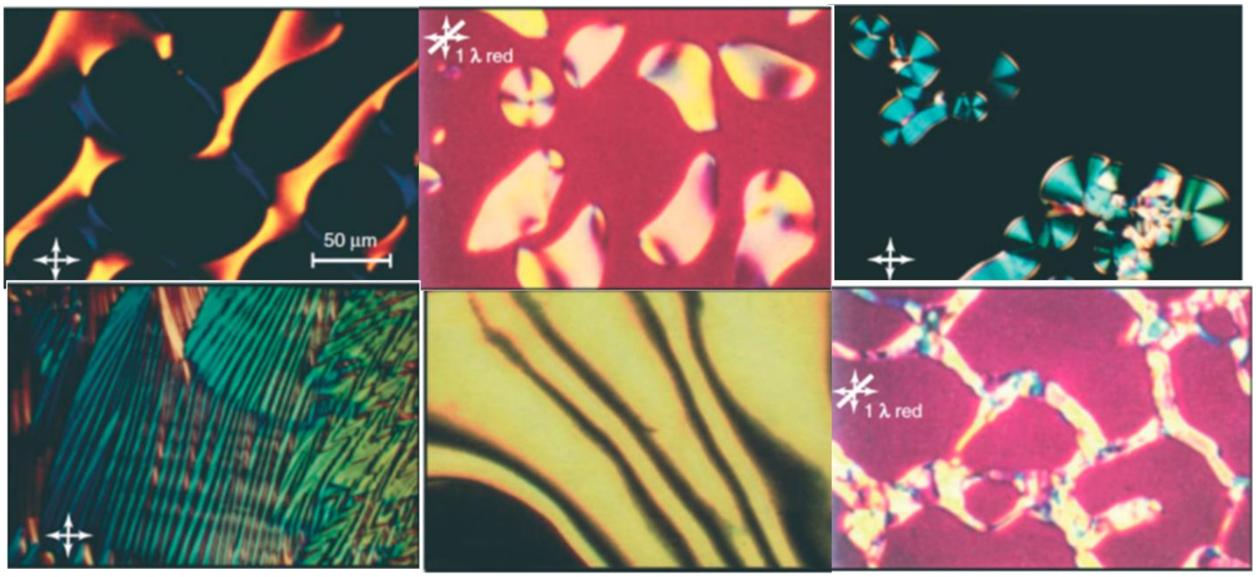


Figure 72. POM images of chromonic mesophases

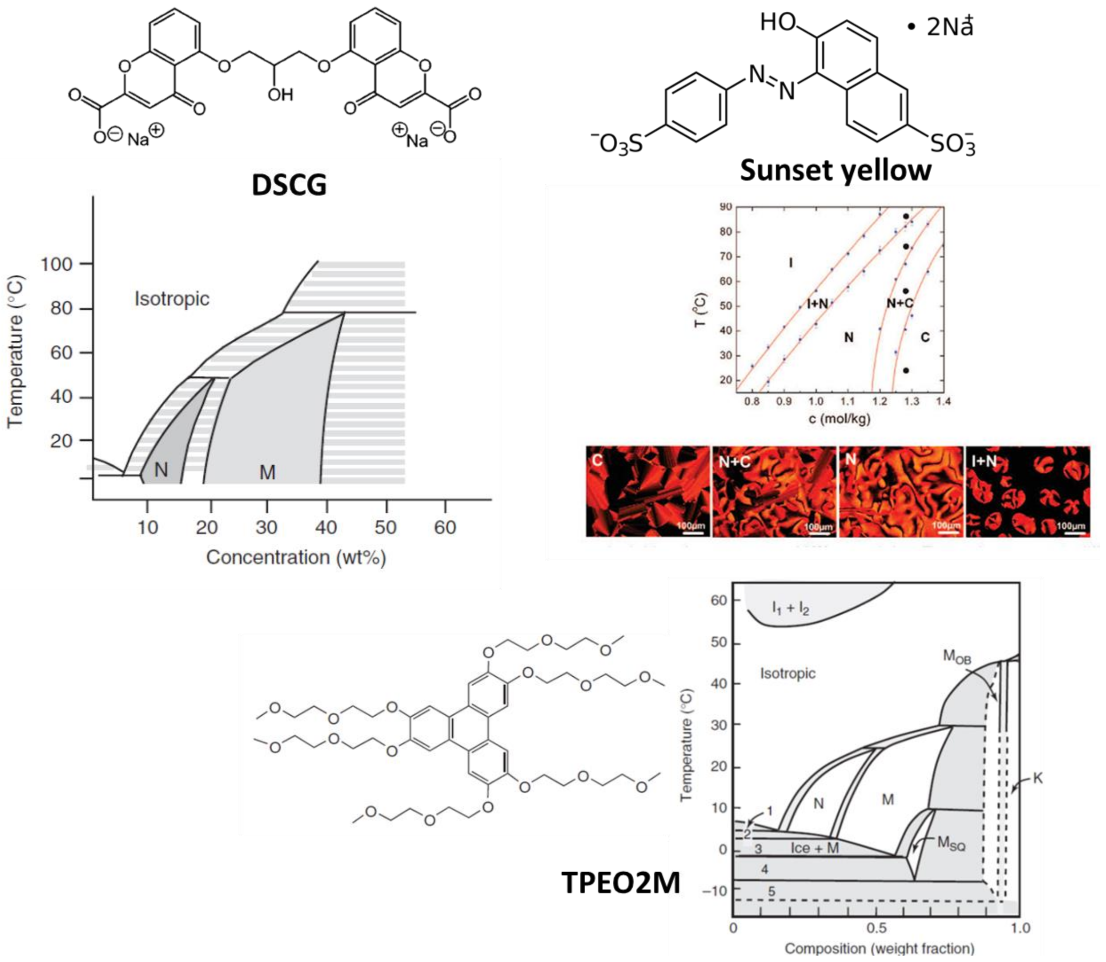


Figure 73. Phase diagram of Representative chromonic mesogens[36]

1.6 Characterization of Liquid crystals:

Liquid crystalline behavior in the material can be studied using the following three techniques

1. Polarizing optical microscopy (POM)

2. Differential scanning calorimetry (DSC)

3. Small-angle X-ray diffraction (SAXS)

This section gives overview of each of the above techniques and their use in Liquid crystals characterization.

1.6.1 Polarising optical microscopy:

Polarizing optical microscopy is a technique widely used to observe the transitions of anisotropic materials. Liquid crystals are one of the anisotropic materials which are characterized using POM studies. The textural pattern obtained from POM serves as one of the main identification of the mesophases involved in a material. Since liquid crystals are birefringent and show the property of double refraction they are visualized through polarized light.

Principle:

Birefringence is the optical behavior, which is well known to be shown by solid materials and the process is essentially the same in liquid crystals. It occurs when light is decomposed into ordinary and extraordinary rays, the ordinary rays will travel parallel to the director and the extraordinary rays will travel perpendicular to the director. This is because the electric and magnetic fields of light (transverse wave of electromagnetic energy) are fluctuating. The two constituent components of the light traveling through the material will travel at different velocities (the ordinary ray travels faster than the extraordinary ray). This arises due to optical anisotropy associated with the liquid crystal phase. The two waves are recombined out of phase with one another after exiting the material, a change in the polarization state occurs

The lightwaves which normally oscillate in random directions are called non-polarized light. Light that oscillates in a single direction is called linearly polarized light. Generally a nonpolarized light on passing through a polarizer (which allows light only in a specific direction as per their optic axis) comes out to be polarized i.e the vibrations are restricted to one plane. When a linear polarized light is passed through the analyzer (which is nothing but a polarizer) whose optic axis is in the perpendicular direction, there will be no light coming through analyzer, as the two polarizers are crossed and no light reaches the eyepiece of microscope.

A birefringent material is the one which has the ability to able to change the plane of polarization of light when it is placed between the two polarizers of a microscope, they allow the light to pass through the analyzer and finally to the eyepiece. On the other hand, non-birefringent material cannot change the polarization of light, so they won't let any light to pass through when they are in between two polarizers under crossed conditions (**Figure 74 & Figure 75**)

Isotropic Liquids:

In an isotropic liquid, refractive index is independent of the direction that the incident light passes through the material, which does not lead to any birefringence. Since liquids are not birefringent, the polarization of light under POM is unaltered after passing through the material, then the light does not come out of analyzer. This characteristic is very useful when darkness results. It is very easy to identify isotropic phase through POM.

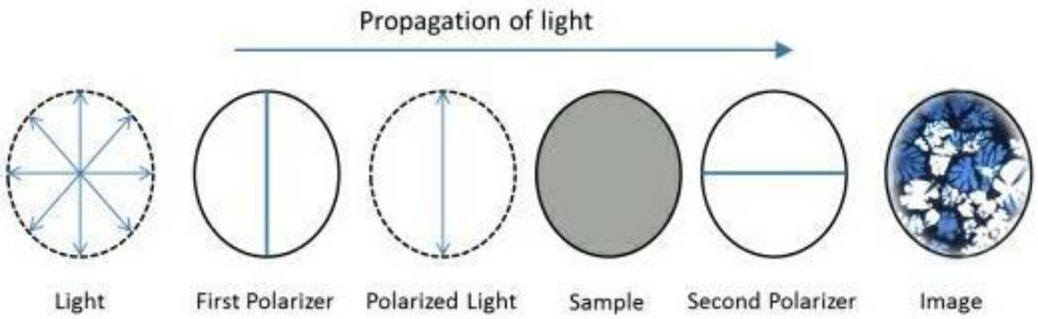


Figure 74. Schematic of Polarizing Microscope

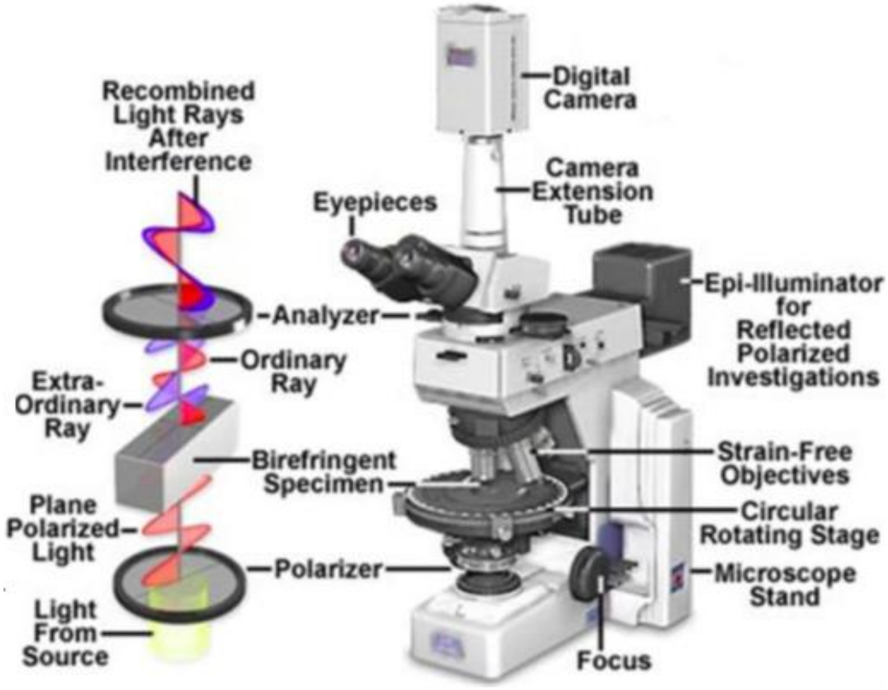


Figure 75. Polarising optical microscope

Liquid crystal phases under POM[37]:

Liquid crystalline materials show birefringence under polarizing microscope due to their anisotropic nature. The anisotropic nature of crystalline and liquid crystalline materials is responsible for the beautiful textures that can be seen under POM. When light enters through a birefringent material, it is broken up into two components; a fast component which is called the ordinary ray (o) and a slow component which is called the extraordinary ray (e). These two components travel with different velocities through the sample and become out of phase. When both the rays recombine as they leave the birefringent material the plane of polarization of the light has been modified because of phase difference.

There are cases where birefringent material will give partially dark or entirely black POM images, (a) When they are Homeotropically aligned: when the molecules aligned with substrate plane in perpendicular direction leads to dark image under POM. The dark image is because the director is aligned with the optic axis of the polarizer.(**Figure 76**)

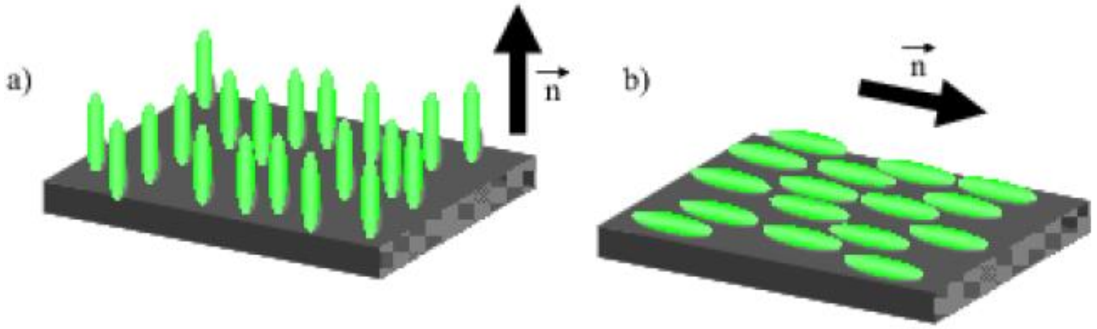


Figure 76. a) Homeotropic alignment; b) Planar alignment

Through POM, it is very easier to distinguish between isotropic liquid, liquid crystalline, and crystalline phases. But distinguishing among different liquid crystal types requires experience and knowledge. Each liquid crystal phase show texture unique to them due to the presence of some of their defect structures which are particular to each one of them. The detail description of all the defect structures is beyond the scope of this chapter. But there is brief account on some of the features of different LC textures under POM are given below

Nematic Textures:

Nematic liquid crystalline phases are named because of thread-like textures (Nematic-The Greek word for ‘thread’). They also give a pattern called Schlieren texture. Schlieren textures are identified by the presence of dark brushes that meet at a single point. The brushes can be two- or four-fold which meet at a point called a singularity. The lines that separate the brushes are called disclination lines. The disclination lines are the outcome of a defect in the orientation of the director. Smectic A LC also found to show schlieren textures but they only fourfold brushes. The presence of two-fold brushes confirms the presence of the nematic phase. (**Figure 77**)

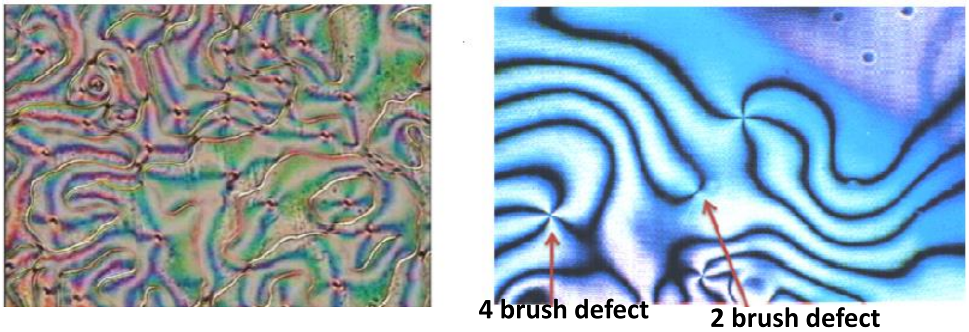


Figure 77. Nematic textures

Cholesteric phases show fingerprint textures, droplets, fan textures (**Figure 78**)

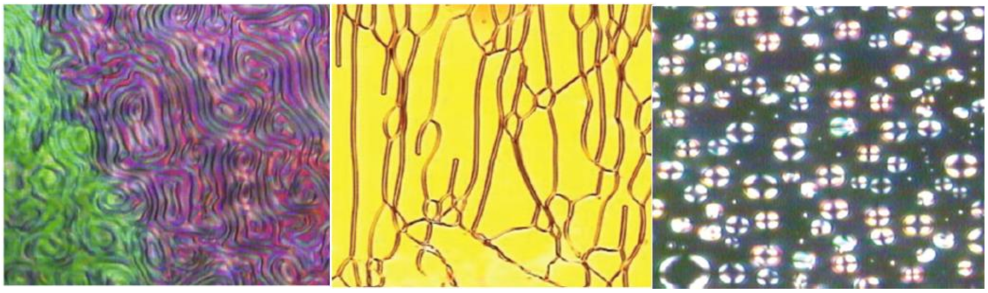


Figure 78. Cholesteric Textures

Smectic Textures

Smectic A phases are one of the most common mesophases observed in diverse compounds ranging from organic, complexes and surfactants. The characteristic textural feature of smectic phases is the formation of batonnets (in French batonnets means sticks). These batonnets appear

on cooling from the isotropic liquid and can persist to a lower temperature or coalesce into other patterns. Sometimes they show fan-shaped texture. They also show oily streaks or focal conic textures.(**Figure 79 & Figure 80**).

Figure 79. Smectic Textures

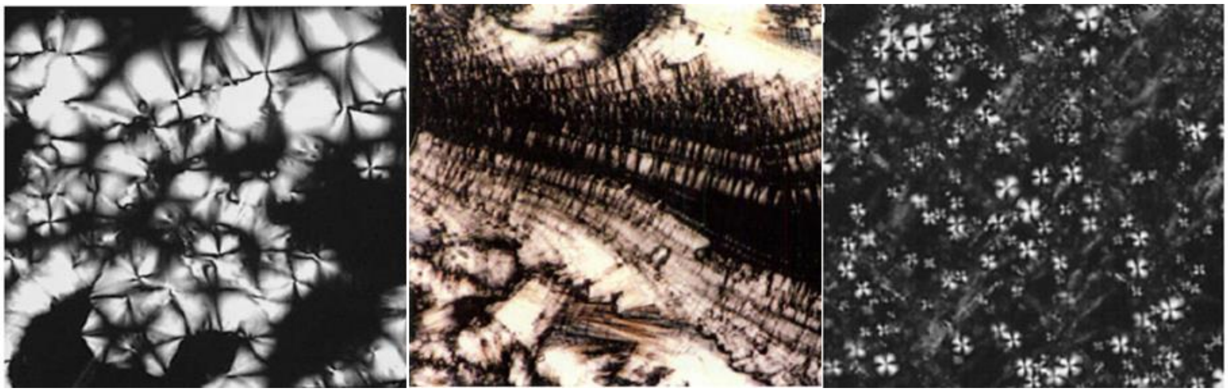


Figure 80. Smectic Textures

Columnar phases:

Columnar phases were found to show fan-shaped structures, one of the commonly observed texture are mosaic texture. They also found to show patterns called dendritic textures.

Collage of Microscope images of liquid crystals[37]:

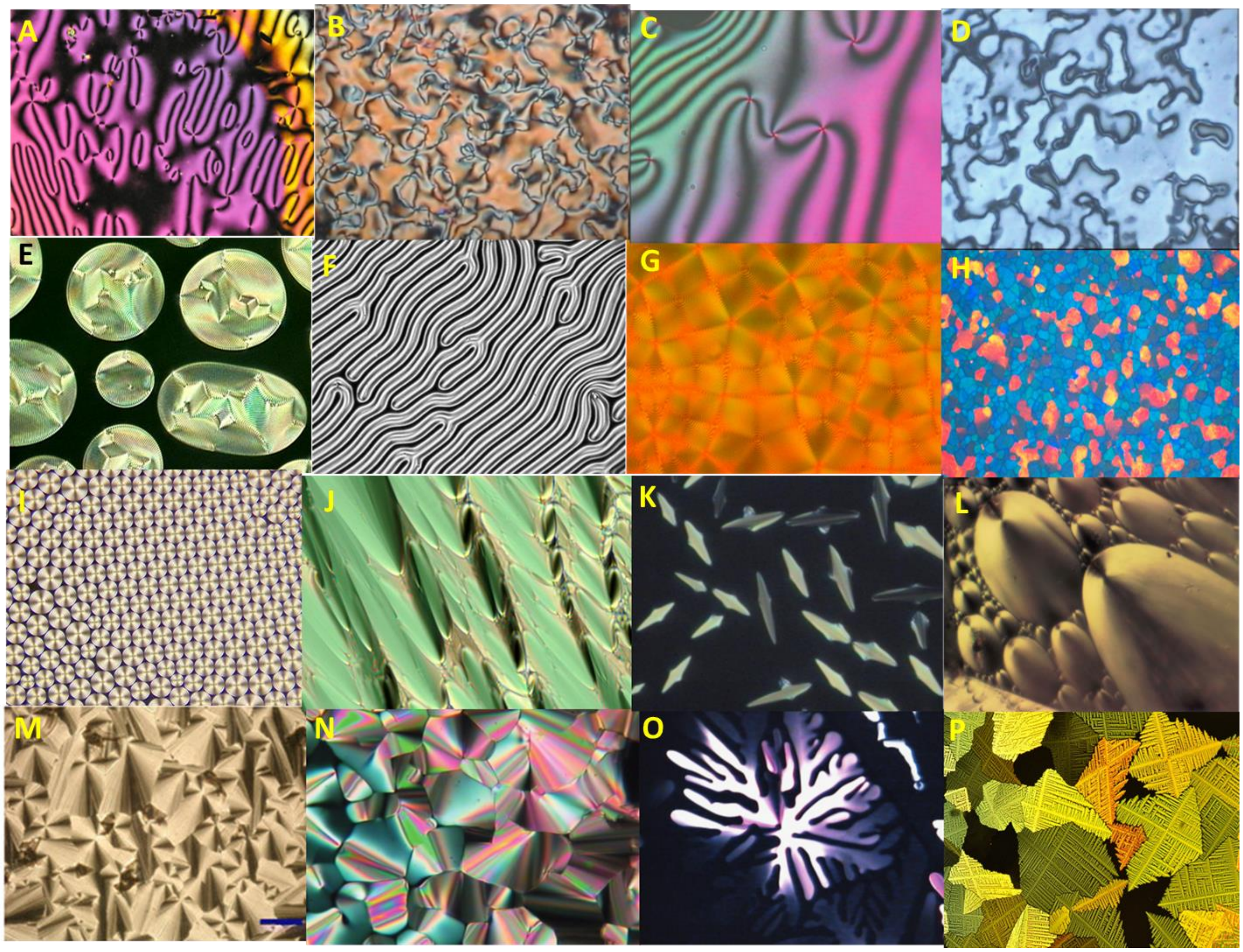


Figure 81:POM images: Nematic textures (A-D); A. schlieren texture; B. Schlieren texture; C Schlieren texture; D. Thread like Textures; Cholestric Textures(E-H); E. Focal conic domains, F. Fingerprint texture, G. polygonal texture, H. Blue phase; Smectic Textures (I-L); I. Focal conic domains, J. Focal conic domains, K. batonnets , L. polygonal textures; Columnar Textures (M-P); M. Focl conic, N. Pseudo focal conic, O. dendritic textures, P. dehydritic texture

1.6.2 Differential scanning calorimetry:

Differential scanning calorimetry is one of the main techniques in characterizing liquid crystals. This technique monitors the phase transitions in the sample induced by variation of temperature through measuring enthalpy involved in a phase transition. When a compound undergoes phase change from crystal to a mesomorphic state, energy is absorbed because of loss of positional and orientational order (disruption of intermolecular forces of attraction), this process will be endothermic in nature. Similarly, energy is released when there is the formation of intermolecular forces (more positional or orientational order, as the compound, transits from a less ordered liquid crystalline to a more ordered crystalline phase. This does not give any information about the nature of the phase. The extent of enthalpy change provides some information about the types of phase involved (through information about order of the phase transition).Eg, SmA to SmC is usually a second-order phase transition associated with low enthalpy.

1.6.2.1 The thermodynamics of the phase transitions[38]:

The phase transitions involved can be classified into two types discontinuous (also called first-order) **&** continuous (also called as second-order). They can be distinguished as follows.

The Gibbs free energy (G) associated with phase transition is defined as:

$$G = H - TS$$

Where H is the enthalpy, T is the absolute temperature and S is entropy.

The first derivative of G with respect to T gives the negative of the entropy, it is shown as follows

$$\left(\frac{dG}{dT}\right)_p = -S$$

The above equation tells that if the entropy at a phase transition shows a discontinuity, then we can decide the order involved in a first-order phase transition. In some cases, there is no change in entropy and enthalpy observed and further, there is a discontinuity in the second derivative which results in a second-order phase transition. The transition between one LC phases to another mostly belongs to first-order transitions with few exceptions Example: smectic C to smectic A.

$$\left(\frac{d^2G}{dT^2}\right)_p = -\frac{C_p}{T}$$

1.6.2.2 Principle:

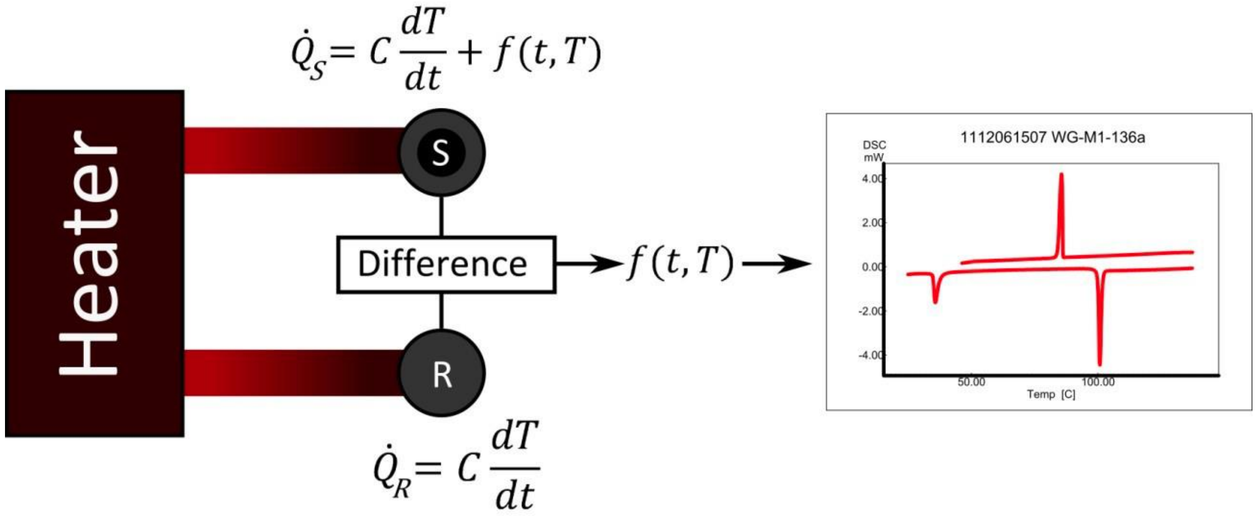


Figure 82. Principle of DSC

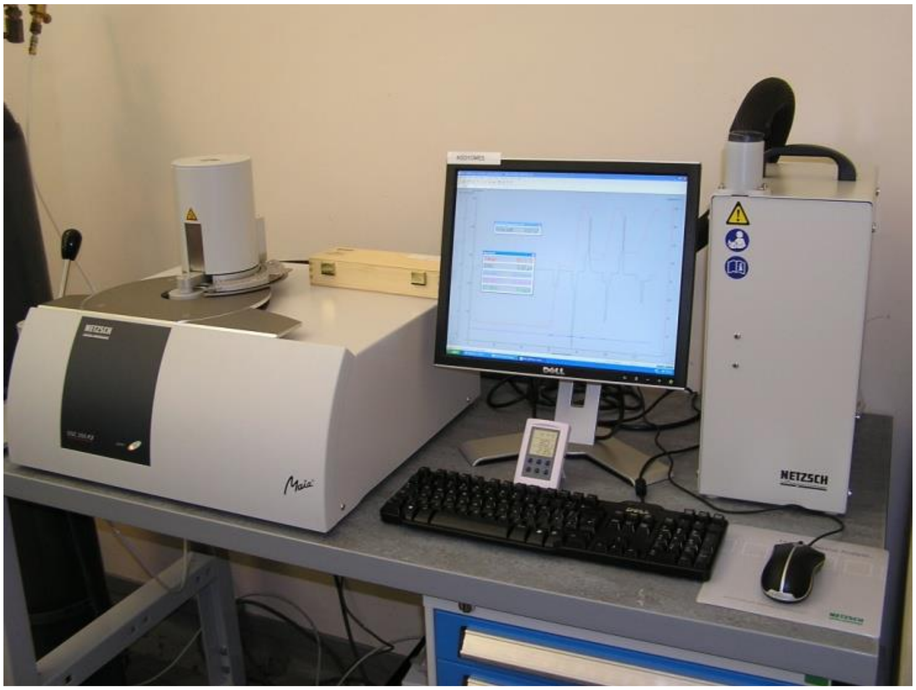


Figure 83. Differential scanning calorimeter

DSC is a technique that measures the difference in heat flow into a sample and an inert reference as a function of raising or lowering the temperature. It is used to monitor changes in the sample which occur due to changes in temperature, such as phase changes.

The heat flow (Q_s) into the sample has two components

$$\dot{Q}_s = C_s \frac{dT}{dt} + f(t, T).$$

The first component describes the heat flow required to change the temperature of the sample. It incorporates the heat capacity of the sample (C_s) and the rate of change of temperature (dT/dt). Under ideal conditions, the first component would be the same in both the inert reference and the sample as their heat capacities would be approximately the same. Consequently, when the differential heat flow is measured, this component is removed leaving behind the second component (in blue) alone. The second term signifies heat flow due to the heat of a transition in the sample.

The DSC thermogram is usually plotted as heat flow in milli watts (mW)as a function of temperature(°C). The output gives peaks for the phase transitions, and the areas under the peaks gives latent heats for the transition. A typical enthalpy change of a crystal – mesophase or isotropic liquid transitions is about 30-50 kJ/mol. This is a good indication that a considerable structural ordering is developing. A much smaller enthalpy change is involved within a mesophase – mesophase, and mesophase – isotropic liquid transitions, usually those have values of less than 10 kJ/mol. The transition temperatures for the phase transitions are read by determining the temperature for the maximum gradient in the heat flow from the peaks in the DSC output.

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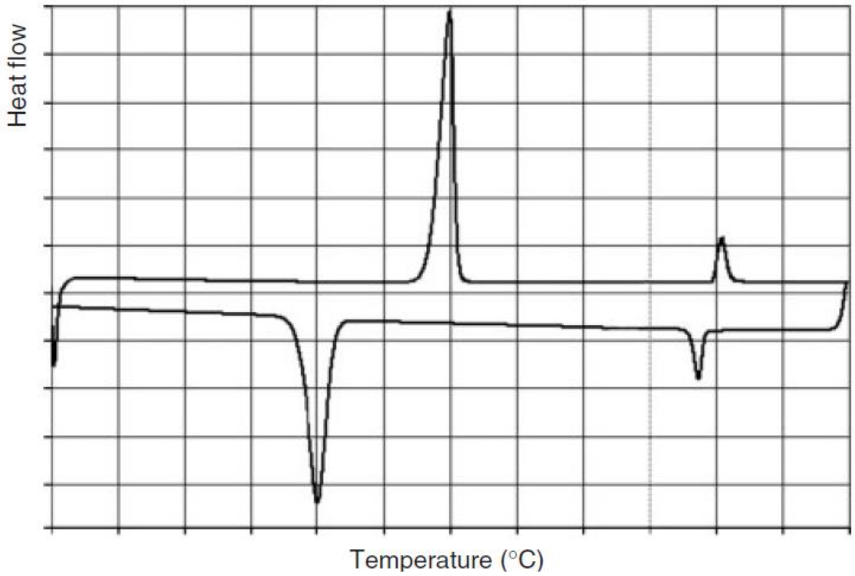

Figure 84: Typical DSC thermogram

Typical enthalpy values[38]

Transition	Enthalpy (KJ/mol
Crystal –Mesophase	117.3
SmC-Isotropic	42.7
SmA-Isotropic	12.6
SmB-SmC	10.5
N-Isotropic	9.64
SmC-Nematic	9.64
SmA-Nematic	4.61
SmA-SmB	4.61

1.6.2.3 Informations given by DSC thermograms:

DSC analysis gives the following quantitative data about the sample

- Peak and onset temperature of phase transitions: the method to calculate onset and peak temperature is shown in the **figure 85**.

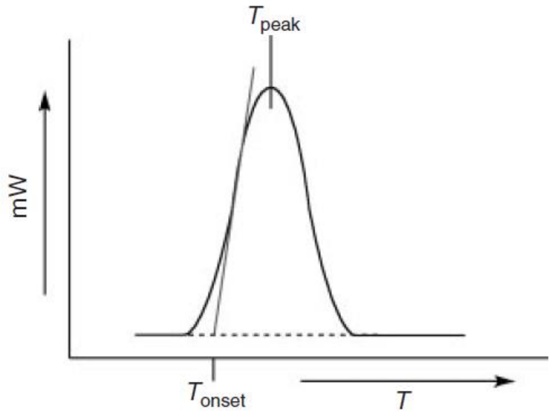

Figure 85. Determination of peak temperature from DSC thermogram

- The entropy change (ΔS) associated with physical changes of LCs may also be calculated from ΔH value (ΔS = ΔH/T). The change in entropy is a measure of the disorder introduced in a certain system. When a crystal, is heated to its melting point, the absorption of heat during the transition state will produce the disruption of the very ordered crystal lattice and passage to a less ordered structure (e.g. mesophase). Hence the melting phenomenon is accompanied by a great increase in the disorder (or entropy) of the system. When less ordered systems, such as a liquid crystal phase, is heated to the clearing point the disruptive effect of the absorbed heat over the transition state is relatively small, with a small additional disorder (small ΔS). In the DSC plot, The area under the peaks will represent a measure of the amount of ΔH (and consequently ΔS) involved in the transitions. Large ΔH are characteristic of great changes in order. Therefore, large areas under the peaks represent crystals to melting transitions since the sample undergoes an appreciable change in the lattice order. Mesophase to mesophase or mesophase to isotropic transitions involve smaller ΔH because the degree of structural order in these phases is quite similar, resulting in small areas under the peaks.

- In order for a material to pass from a crystal to a mesomorphic state, energy is absorbed due to loss of positional and orientational order (break the intermolecular forces of attraction), hence this process is endothermic. On the other hand, energy is released for the formation of intermolecular forces (more positional or orientational order), as material passes from a less ordered mesomorphic state to a more ordered crystal state.

1.6.2.4 Features of DSC

1. Thermograms of enantiotropic systems: They have classically two melting points. The melting point (Crystal - mesophase) has the largest peak. The area under the curve will give enthalpy associated with the transition. Further, the entropy involved in the transition can be calculated by dividing the enthalpy obtained with the temperature associated with phase transition and renormalize with respect to per mole scale. They often show a typical first-order phase transition. Once the liquid crystal phase is formed the thermograms show a flat line indicating the sample is in the liquid crystalline regime (indicates heat capacity associated with the phase). When clearing point is approached, it gives a peak similar to melting transition but with a lower enthalpy typically 5-10 times smaller than melting transition. The cooling process scan is necessary for the sample. During cooling, the sample from isotropic state shows a first peak corresponding to isotropic to LC transition. The position of onset for this transition determines the purity of the sample. The onset temperature should be very similar to that of the equivalent heating peak (around 5 ^{o}C). On further cooling, the crystallization process will happen but the onset point of crystallization won’t be similar to that of the melting found in heating scan. It will be much lower. This is due to supercooling. The enthalpies of both transitions also won’t match. (**Figure 86**)

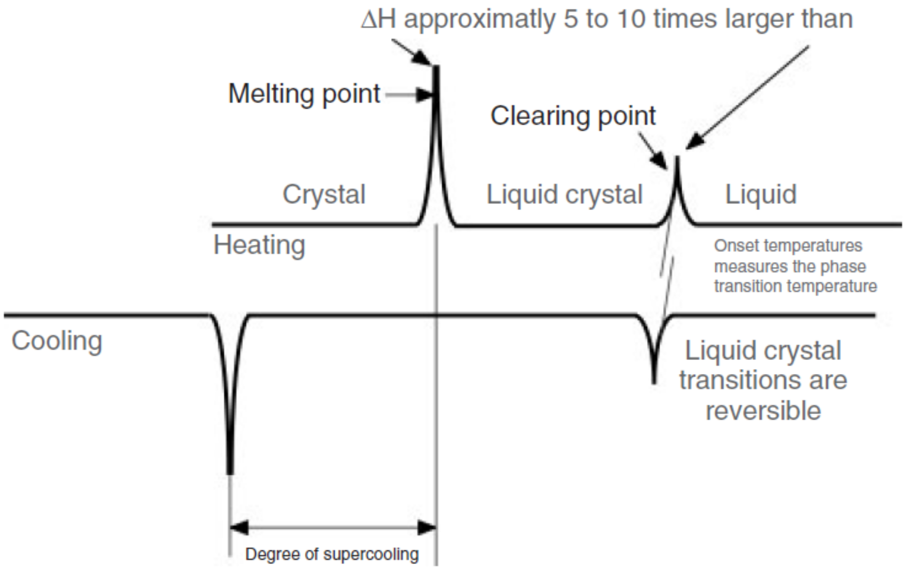

Figure 86. DSC thermogram of enantiotropic systems

The supercooling phenomena can be explained as follows. When a fresh sample is subjected for DSC scan, it was recrystallized from a suitable solvent, which gives rise to sample that is most stable solid-state. On the cooling during DSC scan, the sample reaches the crystalline state via solidification not through recrystallization as the virgin sample. So the reheated compound will have a different melting point.

The below thermogram gives an example of the sample with multiple enantiotropic transitions (**Figure 87**). The peaks are assigned as for the crystal E to smectic B, smectic B to smectic A, and smectic A to the isotropic liquid transitions respectively and all of them are first-order transitions. They have small but perceptible latent heats values associated with them. The enthalpy for the melting point is clearly larger than for the other three peaks combined, indicating that the associated enthalpy corresponds to the crystal lattice melting.

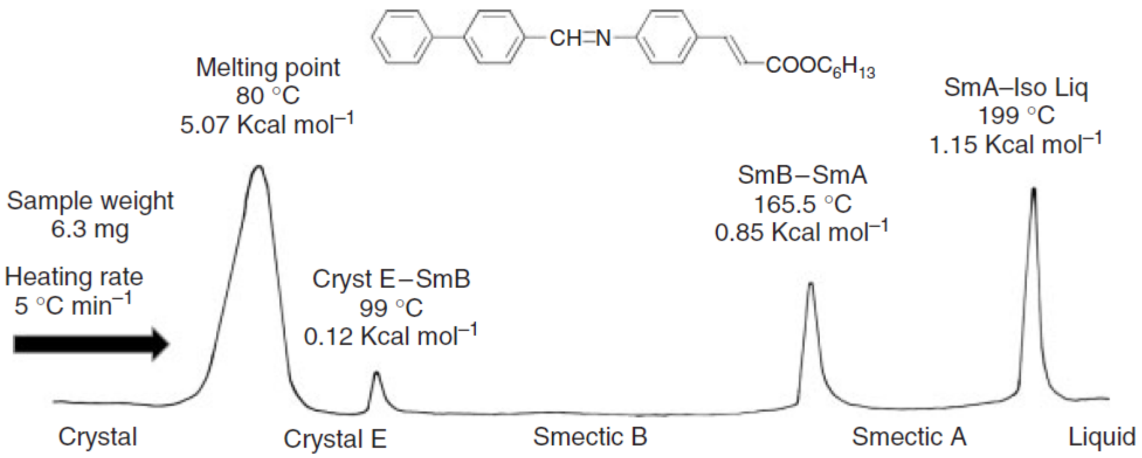

Figure 87. DSC thermogram with multiple enantiotropic transitions

2. Crystal to crystal transitions: The below thermogram shows crystal to crystal transitions before the melting process to liquid crystal phase. The enthalpy involved also found to be smaller than melting transition. The transition with the highest melting point gives the true melting point of the sample. Since at that point the crystal lattice collapses to give the soft crystal phase. So the crystal–crystal transition, therefore, corresponds to a transition associated with change in the lattice structure (**Figure 88**)

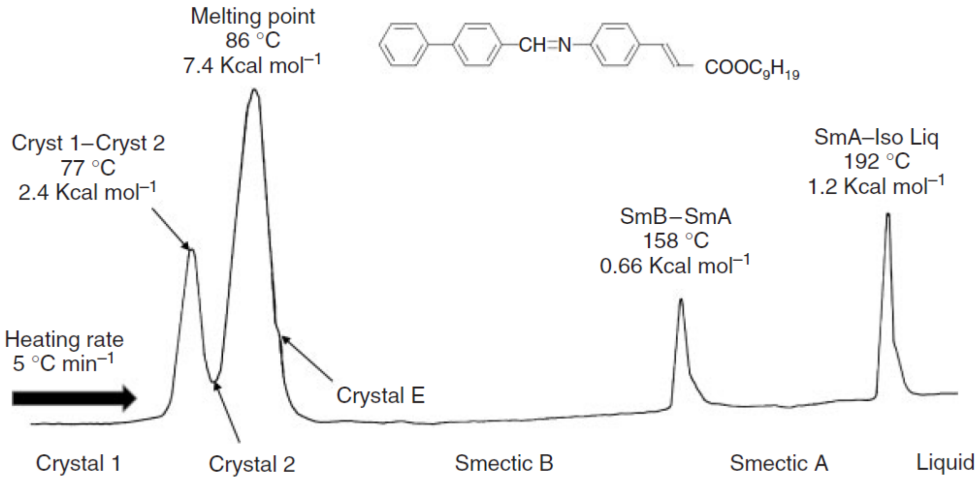

Figure 88. DSC thermogram for melting tarnsitions

3. Monotropic transitions:

Monotropic LCs generally have seen below the melting point and show supercooling of the formation of solid-state. The following thermogram (**Figure 89**)gives an idea about monotropic transitions. Here there are two enantiotropic transitions 1&2. The range involving LC 1 is the same on both heating and cooling, but for LC 2, In the cooling cycle, the temperature range differs from that of heating. This can be accounted for the formation of a third transition called a monotropic transition. On repeated cycles of heating and cooling to find out the transition details of 2-3.In order to get the details regarding the transition of 2 to 3. The cooling scan will be stopped just after the transition is observed and reheat the sample. This will give us the temperature corresponding to the monotropic transition.

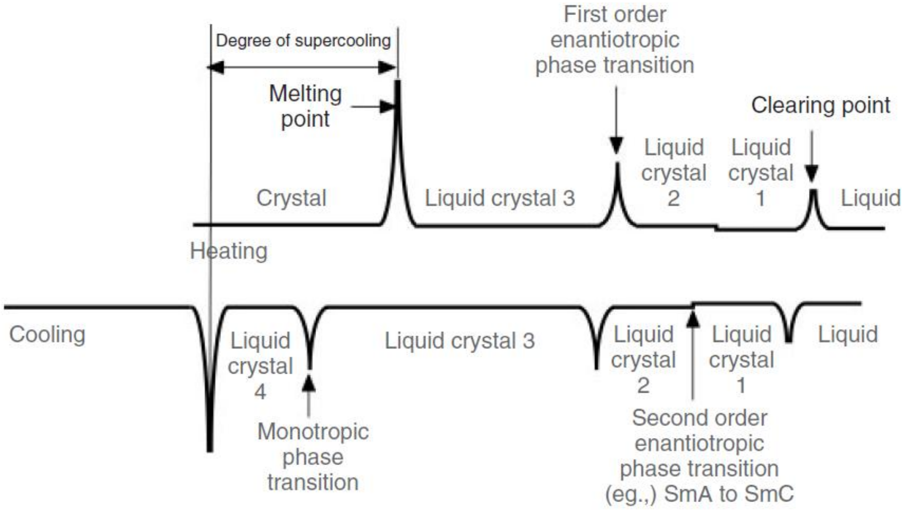

Figure 89. DSC thermogram for Monotropic transitions

4. Second-order transitions: Smectic C to smectic A phase transition is found to be second order. Generally, they show a step in the baseline of thermogram. This observation can be accounted as follows, the transition does not have enthalpy change associated with them but the transition will be having a change in heat capacity (**Figure 90**). The following thermogram illustrates the second-order transition. The material was found to have four mesophases: (three are first order, among three one is monotropic, one is second order.) In reporting the second-order phase transition, the temperature for the phase change should be given but not the associated enthalpy.

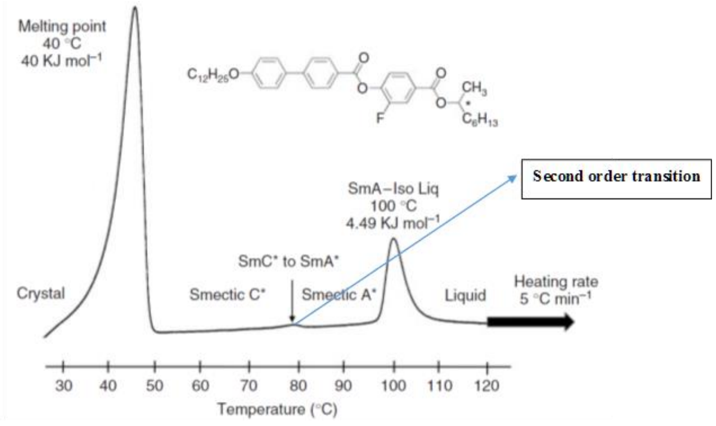

Figure 90. DSC thermogram for Second-order phase transitions

5. **Glass transitions:** The phenomena of glassification is often found in polymeric systems. Glassification results when there is dampening in the motion of polymer backbone. Liquid crystalline polymers, the dampening motion of polymer backbone and mesogenic motif are not coupled, further, they are often disordered enough so the possibility of crystallization will be a rarity. When a dampening motion of polymer does not take place at a particular temperature, and there is no formation of solid lattice there will be no enthalpy involved in the process. But there will be heat capacity associated with the motion which results in a shift in the baseline of thermogram. The maximum change in gradient will be termed as glass transition temperature (T_g). (**Figure 91**)

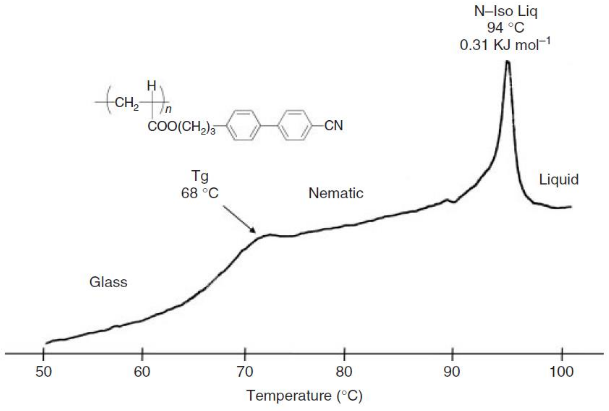

Figure 91. DSC thermogram for Glass transition

1.6.3 X-ray diffraction[39]:

Crystallography deals with diffraction of x-ray or neutron beams by a crystalline material. These analytical techniques are very much vital for studying the morphology of crystalline systems. Neutron or x-ray diffraction involves the analysis of systems containing arrangements of atoms, molecules or particles in an ordered array. This orderly arrangement in a crystalline material is known as the crystal structure, with the term “unit cell” used to describe the smallest structure that repeats itself by translation through the crystal

1.6.3.1 Braggs law:

Bragg’s law gives geometrical conditions of scattering of X-rays which can produce the maximum intensity of diffraction peaks. The figure demonstrates the scattering of X-rays caused by atoms in a crystal lattice. X-rays are incident on atoms with the angle of incidence θ and are scattered in all directions. The maximum intensity of diffraction peaks (i.e. Bragg peaks) will be obtained only when the angle of incidence and the angle of scattering of X-rays are equal (**Figure 92**, **Figure 93**).

Figure 92 X-ray diffractometer

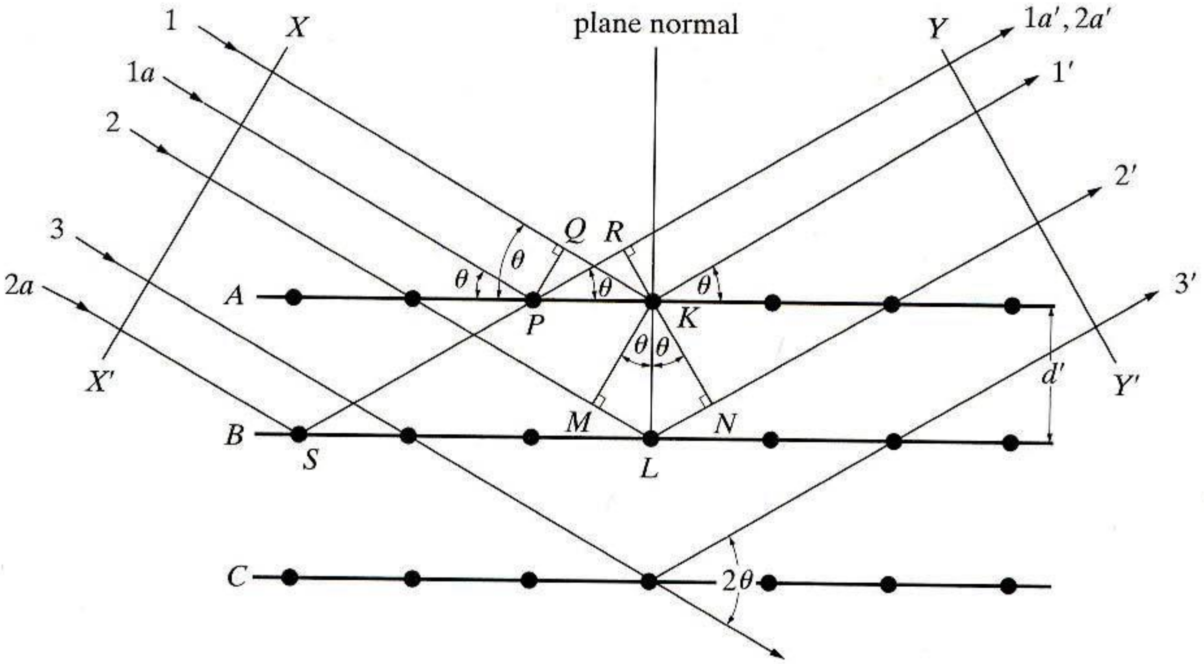

Figure 93. Braggs Law

The path difference between any two rays, rays 1*K*1' and 2*L*2', is a multiple of X-ray wavelength

Path difference between 1K1' and 2L2'= MN+LN = d sinθ+d sinθ

The maximum intensity of diffraction peaks will be obtained only if the path difference between two rays is an integral multiple of the wavelength

$$2d_{hkl} \sin\theta_B = n\lambda$$

Where θ_B = Bragg angle

d_{hkl}= Interplanar spacing of (hkl) plane

λ = Wavelength; n = Integer

We can represent the diffractogram also in terms of q vs I plot where the scattering vector ***q*** represents the space separation of liquid crystal molecules or subunits ($\boldsymbol{q} = 2\pi / \boldsymbol{d}$). The larger magnitude of ***q*** indicates stronger diffraction, corresponding to smaller space distance ***d***.

The Bragg condition implies that the scattering observed at any angle is inversely related to the separation between the moieties constituting the particular phase. This can be explained as follows The diffraction patterns recorded toward the outer edges of an image plate detector correspond to a shorter dimension (typically the lateral separation between the molecules) and the ones which are seen near the center of the image plate correspond to a longer dimension (typically the length of the molecules). The sharpness of diffractograms peaks (FWHM) is considered to be a qualitative measure of order present in the system. The following section gives a brief account of the diffraction patterns of commonly observed phases in liquid crystalline systems.

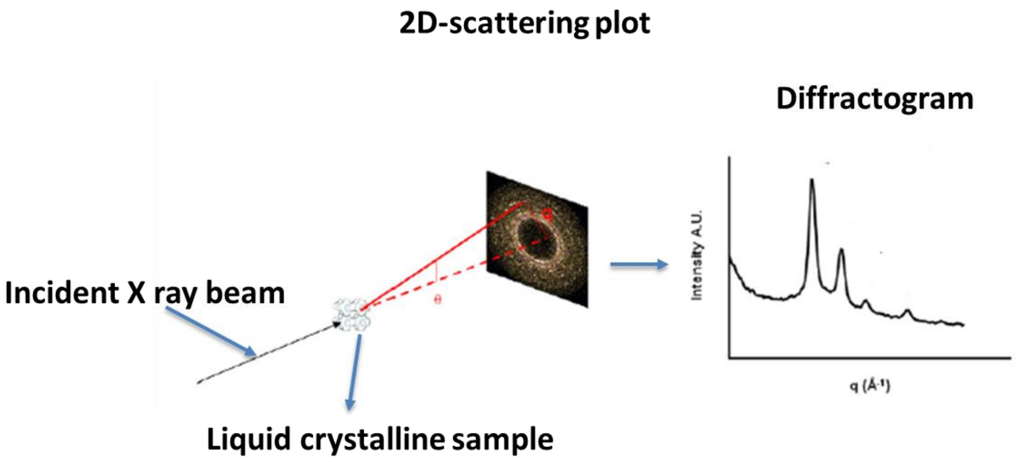

Figure 94. Schematic of diffraction setup for characterizing liquid crystalline samples

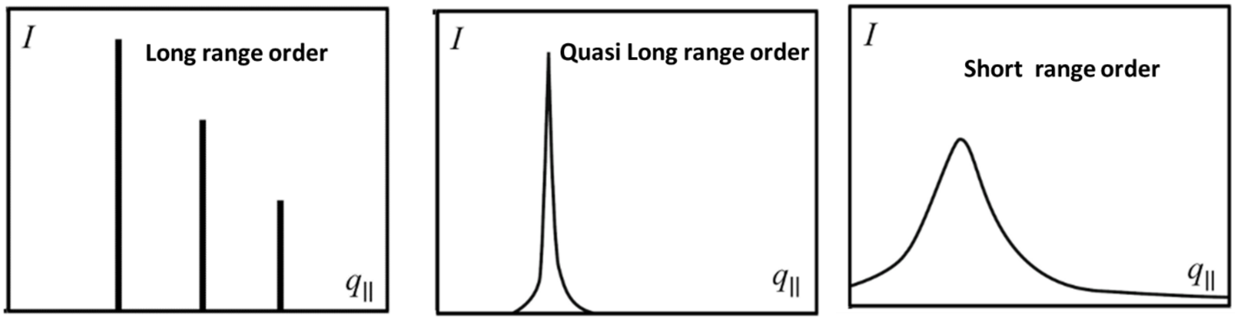

Figure 95. Diffraction patterns for various degrees of order in the system

1.6.3.2 Diffraction patterns from liquid crystalline systems[40]:

Since liquid crystalline systems constitute ordered fused pi-systems and disordered flexible tails. Generally, a liquid crystalline system shows the following feature in diffraction experiments. The molecule constituting aromatic cores can be perfectly ordered with highly disordered tails, resulting in a sharp diffraction peak at $q=2\pi/$ (inter-core spacing) and a broad diffuse maximum at $q=2\pi/$ (mean interchain spacing).

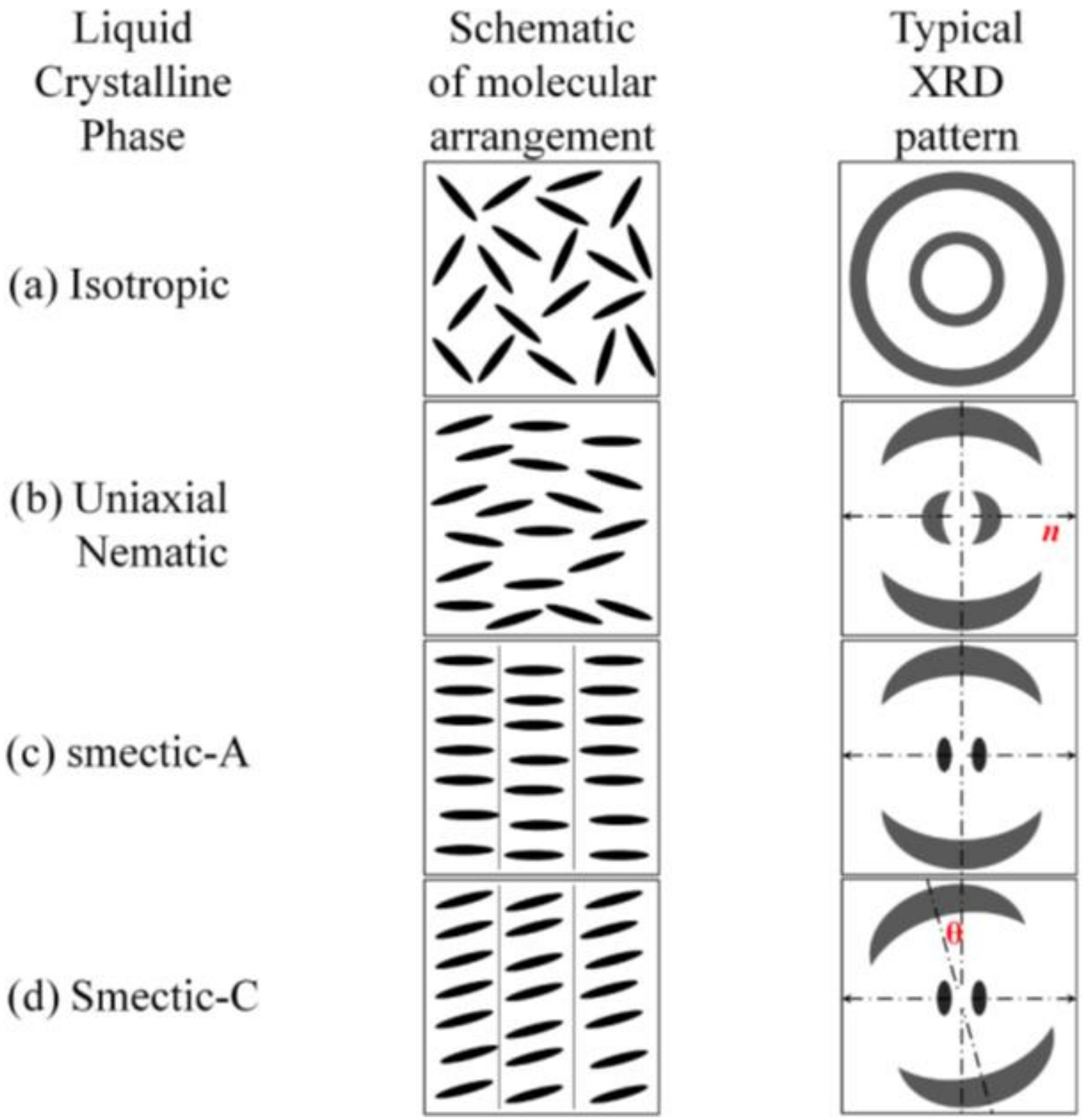

Figure 96. Schematic of diffraction patterns for different Mesophases

1.6.3.2.1 Isotropic:

In the isotropic phase, molecules are all randomly distributed. Isotropic phase gives two rings (one n small-angle region, one in the wide-angle region) in the pattern which are associated with longitudinal and lateral separation between the mesogenic molecules. The isotropic phase is always associated with short-range position order which can be justified by the appearances of two broad peaks (**Figure 97**).

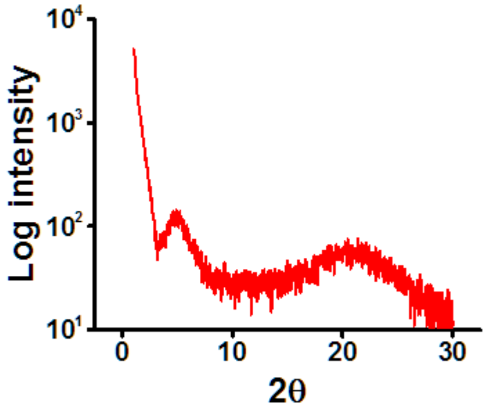

Figure 97. Diffractogram for isotropic samples

1.6.3.2.2 Nematic:

On comparing isotropic with the nematic phase, the loss of rotational symmetry along an axis is the main difference. As mentioned before the nematic phase has long-range orientational order with shorter ranged positional order. In an unaligned sample with a nematic phase, the pattern will look similar to that of an isotropic phase. But the aligned samples do give considerable difference between the two phases. The typical pattern is shown in the **figure 98**.

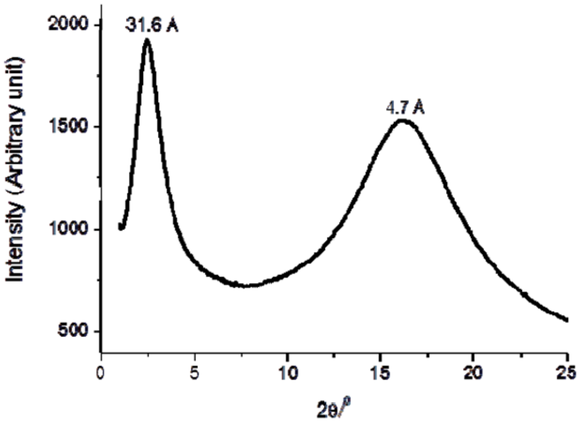

Figure 98. Diffractogram for nematic phase

1.6.3.2.3 Smectic:

Smectic A:

Smectic phases are an arrangement which involves the presence of position order along one direction. They usually assemble in layers. Where within layers the molecules have liquid-like movement but their movement is restricted in a direction perpendicular to layers. The presence of a one-dimensional translational order gives sharp peaks in the small-angle region with their spacings in the ratio 1:2:3. The presence of broad halo in the wide-angle region confirms fluid-like arrangement within layers. (**Figure 99**)

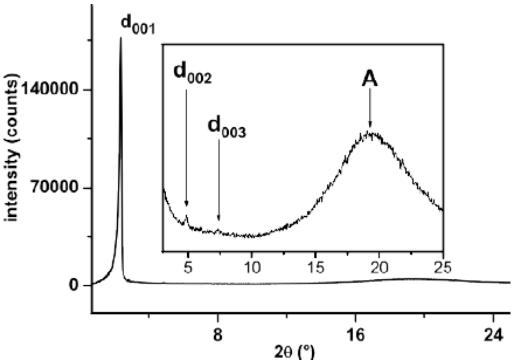

Figure 99. Diffractogram for smectic phase

Smectic C:

A smectic-C (SmC) phase has similar translational symmetry as smectic-A(SmA) phase but differs in their rotational symmetry. The molecules are arranged in the SmC phase in such a way that they are tilted with respect to the layer normal. In an aligned sample, the distinction between the SmA and SmC phases can be made from the angular separation between the large and small angle reflections. The wide-angle peaks rotate by an angle which is equal to tilt angle with respect to small-angle reflection (**Figure 100**). The tilt in the molecular arrangement can be reflected in the decrease in the spacing too with respect to smectic A spacing.

.Both the spacings are related by the following formula

$$\mathbf{d_{Smc} = d_{SmA} * \cos\theta}$$

1.6.3.2.4 Columnar Phase[40]:

Columnar phases are generally shown by disc-shaped molecules. The diffraction pattern of the columnar phase can be described as follows. In the wide-angle region, they give chain correlation peak as the other phases mentioned above. Apart from the fluid peak they also show sharp and diffuse peak corresponding to core-core correlation peak within columns. Typical core–core distances are of the order of 3.5–3.8 Å, and mean fluid chain -chain distances are often of the order of 4.5 Å. In small-angle regions, they often show a series of sharp reflections corresponding to periodic lattice comprised by columns. The positions of these small-angle Bragg peaks are completely a function of symmetry of the columnar lattice (**Figure 100**). The diffraction pattern of different columnar phases is given under the discotic section.

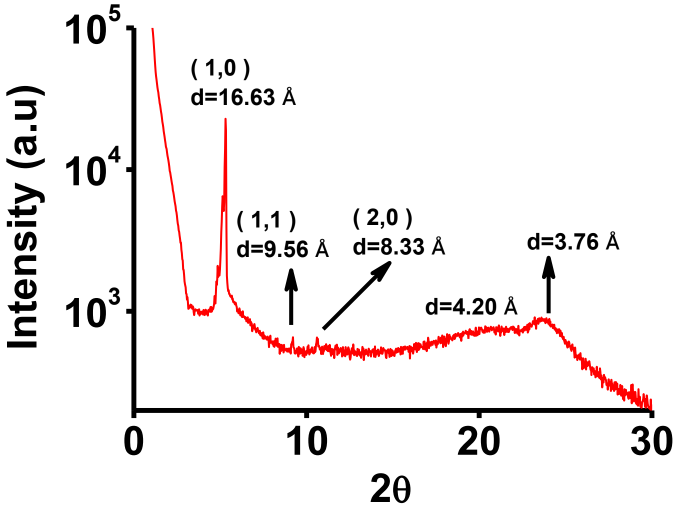

Figure 100. Diffractogram for columnar phase

In some cases, the core- core peak intensity is less compared with fluidity peak which sometimes leads to the absence of any distinct reflection. The sharpness corresponding to core-core peak is a function of correlation length of intracolumnar order. Sometimes patterns with broad or unnoticeable core -core peak can are described as disordered columnar phase. The sharper core core peaks are defined as ordered columnar lattice. Sometimes the series of sharper peaks appear in the wide-angle regions. The indexation of those peaks gives an indication of the presence of 3D crystalline order (**Figure 101**).

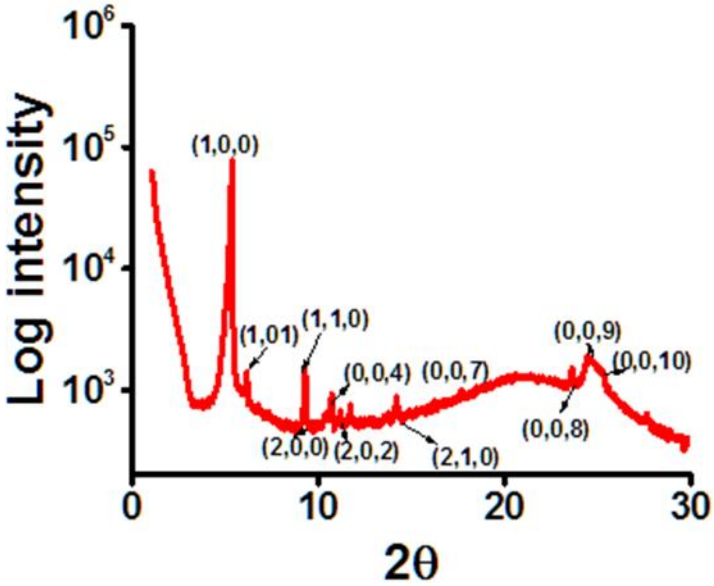

Figure 101. Diffractogram for columnar plastic phase

Columnar phases shown by mesogens of other shapes (pyramidal, hollow-tube, or helical structures), cannot be simply distinguished through the measurements of peak positions alone. The local structural order manifests in the relative intensities of the different peaks.

XRD can be used to identify helical structure only in the case of aligned samples. The characteristic signature of the short-range helical order along a chain or column is a series of diffuse layer lines forming an X-shaped pattern .But, the presence of off-axis diffuse features does not by itself prove the existence of helical order, as there are other morphologies that give similar features in their diffraction studies. The confirmation of the presence of helical order need a rigorous quantitative analysis.

1.7 References and notes:

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