

Chapter 1

General Introduction

1.1 Liquid Crystals

Liquid crystals represent a state of matter intermediate between the solid and liquid phase. They have been defined as “orientationally ordered” liquids or “positionally disordered” crystals with combined properties of both the crystalline and the liquid states¹. Most solids when heated directly change into liquid state, however certain solids do not change directly into liquid state on heating, but pass through phases which have properties intermediate between solids and liquids. Compounds that exhibit these phases are called liquid crystals. Schematic melting behaviour of a liquid crystal² is given in Figure 1.1.

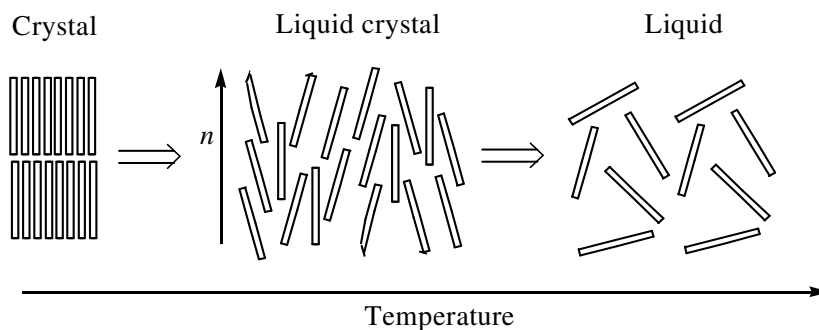


Figure 1.1 Schematic melting behaviour of a liquid crystal

A liquid crystal molecule is called a mesogen and the different phases it forms are mesophases. Liquid crystal mesophases are fluids, which due to partial orientational ordering of the constituent molecules, have material properties such as permittivity, refractive index, elasticity and viscosity which are anisotropic (i.e., their magnitude will differ from one direction to another).

1.2 Classification

Liquid crystalline (mesogenic) compounds can be differentiated into thermotropic, and lyotropic³. Thermotropic liquid crystals change phase with temperature. The transition from the crystalline solid to the mesophase is often termed as the melting point, while that from the highest mesophase to the isotropic liquid is called the clearing point. The mesophases often appear turbid while the isotropic liquid is clear. Thermotropic liquid crystals change phase upon heating or cooling. When the mesophase is obtained by heating the crystalline solid as well as by cooling the isotropic liquid, the mesophase is said to be enantiotropic. Sometimes however, it is only possible to obtain a mesophase by cooling the isotropic liquid. Such a mesophase is said to be monotropic. Lyotropic phases are formed by molecules in a solvent (generally water), and the concentration as well as the temperature control the appearance of the mesophase. Soap is an everyday example of a lyotropic liquid crystal.

Thermotropics can be further subdivided into two main groups, depending on their structural features. Liquid-crystal mesophases may be classified on the basis of the shape of the molecules, which give rise to the properties of the phase. The rod-like molecules are calamitic and the disc-like molecules are discotic⁴. Calamitic compounds have a structure in which the axial part is larger than the radial part (Figure 1.2).

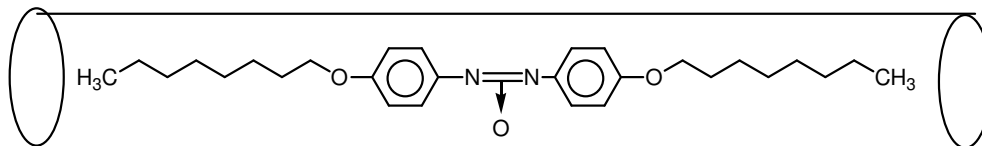


Figure 1.2 Example of a calamitic (rod-like) liquid crystal

Discotic compounds are disc-like as the name implies. The radial parts are larger than the axial part (Figure 1.3).

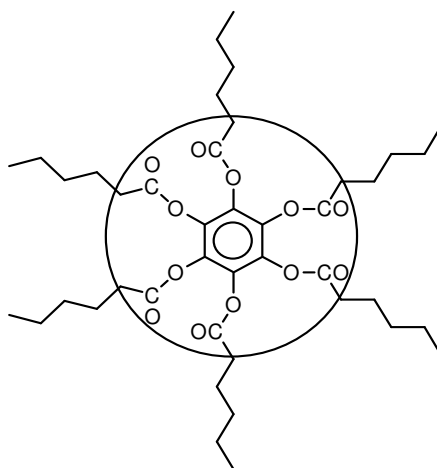


Figure 1.3 Example of a discotic liquid crystal

1.2.1 Calamitic phases

Rod-like molecules can form calamitic mesophases. There are two types of calamitic mesophases; nematic mesophase and smectic mesophase^{5,6}. The less ordered mesophase is the nematic mesophase (N). In this, the molecules align with their long molecular axis more or less parallel to a preferred direction indicated by the director, n (Figure 1.4). The molecules can move freely within the nematic phase and are able to rotate around the long molecular axis.

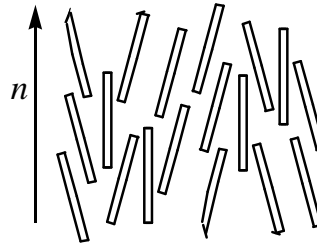


Figure 1.4 Schematic representation of a nematic phase

The nematic liquid-crystalline phase is technologically the most important among the many different mesophases. It is virtually used in all commercially available liquid crystal displays (LCD).

Smectic mesophases (Sm) show a higher degree of order than the nematic phase. There is orientational order as well as some positional order. The molecules are not only oriented in one direction, but also positioned to one another in layers. A number of smectic phases exist which differ in the degree of order present both within and between the layers.

The simplest smectic phase is the smectic A (SmA) phase, in which the molecules are aligned parallel to the normal without having positional order within the layer. In smectic C (SmC) phase, the normal to the layers is tilted by an angle other than 90° (Figure 1.5).

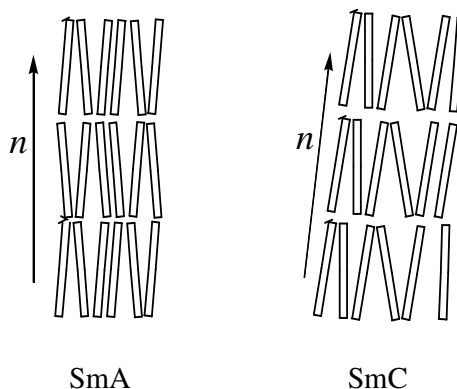


Figure 1.5 Schematic representation of smectic A and smectic C phases

1.2.2 Discotic mesophases

Materials that generate discotic mesophases have a disc-like molecular structure⁸. There are two different classes of discotic mesophases, nematic and columnar. The simplest one is the discotic nematic phase, which has orientational order but no positional order. The discotic nematic phase is denoted by N_D where the subscript D is used to avoid confusion with the normal nematic phase. The discotic nematic phase, like its analogue, is the least ordered liquid crystalline phase. Most of the molecules in the columnar discotic phase tend to position themselves in columns, the different columns constituting a two-dimensional lattice. There are several types of columnar mesophases because of the different symmetry classes of the two-dimensional lattice of columns and the order or the disorder of the molecules stacking within the columns. Examples of nematic columnar phase (N_C) and hexagonal columnar phase (Col_h) are shown in Figure 1.6.

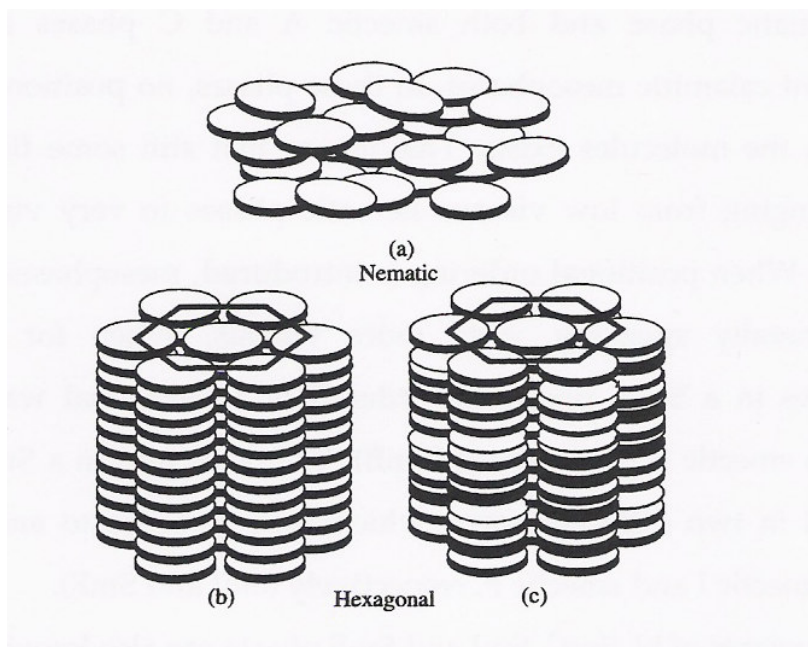


Figure 1.6 Discotic nematic and hexagonal columnar phases¹⁰

1.3 Mesophase characterization

There are three main techniques to identify the liquid-crystalline properties of a compound^{8,9}. The first technique is based on the birefringence of the mesophase and is called Hot-stage Polarizing Optical Microscopy (POM). It is used to look at the optical textures that are typical for a given mesophase. The second technique that is used complimentary to POM is Differential Scanning Calorimetry (DSC). DSC reveals the phase transition temperatures as well as transition enthalpies. A third way to study mesogenic behaviour is by using X-ray Powder Diffraction (XRD). When an X-ray beam interacts with the typical structure of the mesophase, a characteristic diffraction pattern is observed, which allows identification of the mesophase.

1.3.1 Hot-stage Polarizing Optical Microscopy (POM)

This technique is based on the fact that the mesophase is anisotropic and birefringent. This means that the mesophase has two different refractive indices, parallel and perpendicular to the liquid crystal's director. When the sample, in its liquid-crystalline state, is struck by a polarized beam of light two refracted rays are formed, which interact with each other to give a typical pattern under the microscope. This pattern is called texture and is different for each mesophase. A schematic representation of polarizing optical microscopy is depicted in Figure 1.7.

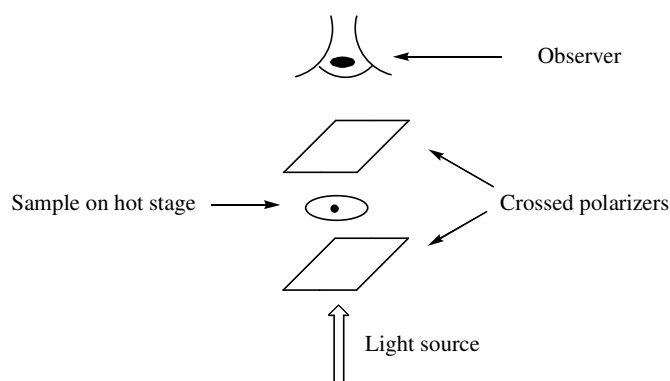


Figure 1.7 Schematic representation of Polarizing Optical Microscopy (POM)

A small amount, approximately 1-2 mg of the sample, is placed between two microscope cover slips and is positioned on the hot stage. This hot stage is made of silver, because of its high thermal conductivity, and can be heated or cooled by means of a computer-driven temperature controller. The microscope is equipped with two polarizers; one is placed between the light source and the hot stage and the other is localized between the hot stage and the observer. The polarizers can be rotated, but are typically placed in a crossed configuration. This means their

polarization directions are perpendicular. In this way, only birefringent materials, like most mesophases, can cause an image to appear. Isotropic materials, like the isotropic molten phase, are not birefringent and therefore cannot cause an image to occur.

The best textures are obtained when the sample is cooled from the isotropic liquid. These are called natural textures. The sequence in which the different textures are observed upon heating or cooling can also be diagnostic for the mesophase transitions. The natural texture of a nematic phase (N) occurred when 4-nonyloxybenzoic acid is cooled from the isotropic phase (Figure 1.8)¹⁰.

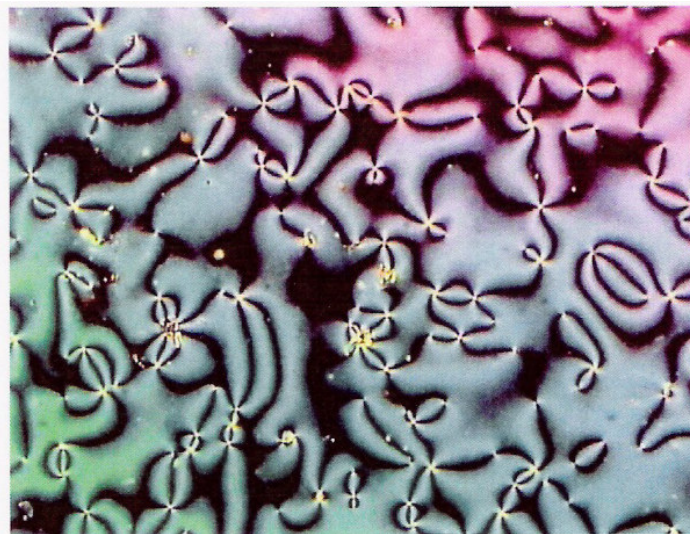


Figure 1.8 Schlieren texture of a nematic phase¹⁰

Typical characteristics for a nematic phase is the presence of dark brushes called Schlieren, which seem to emerge from bright spots in the texture. These ‘spots’

are called singularities and are formed when areas of differently oriented molecules collide. A typical picture of smectic A is given (Figure 1.9).

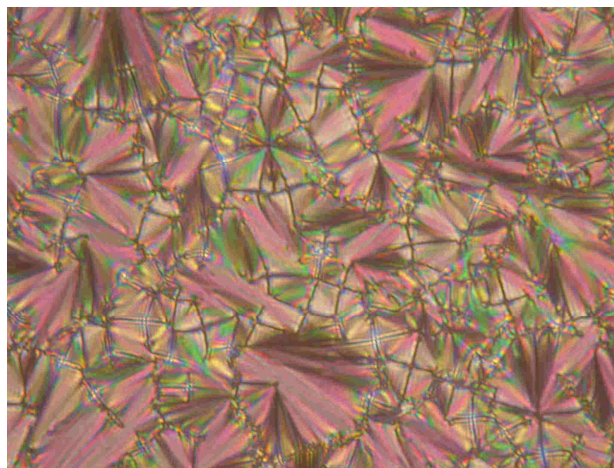


Figure 1.9 Texture of a smectic A phase¹¹

The fan-shaped texture occurs when cooling from the isotropic liquid. During the cooling, rod-like features appear first and these are called batonnets. Gradually these batonnets coalesce to form the fan-shaped texture. A typical texture of a hexagonal phase is shown in Figure 1.10.

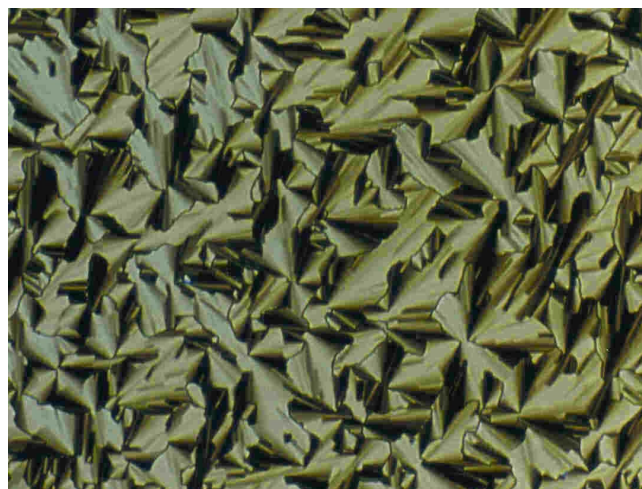


Figure 1.10 Texture of a hexagonal phase¹¹

Hexagonal columnar phase is different from the textures of nematic phase and smectic phase.

1.3.2 Differential Scanning Calorimetry (DSC)

Many physical or chemical transformations are associated with heat absorption (endothermic) or heat evolution (exothermic). These events are easily detected by a difference in temperature and heat flow between a sample and an inert reference material. Since liquid crystals show physical and/or chemical transformations by increasing the temperature, which involve a change in enthalpy or heat capacity, DSC is a widely used technique in the investigation of the thermal behavior of these compounds. A DSC thermogram of 4-nonyloxybenzoic acid² is given in Figure 1.11.

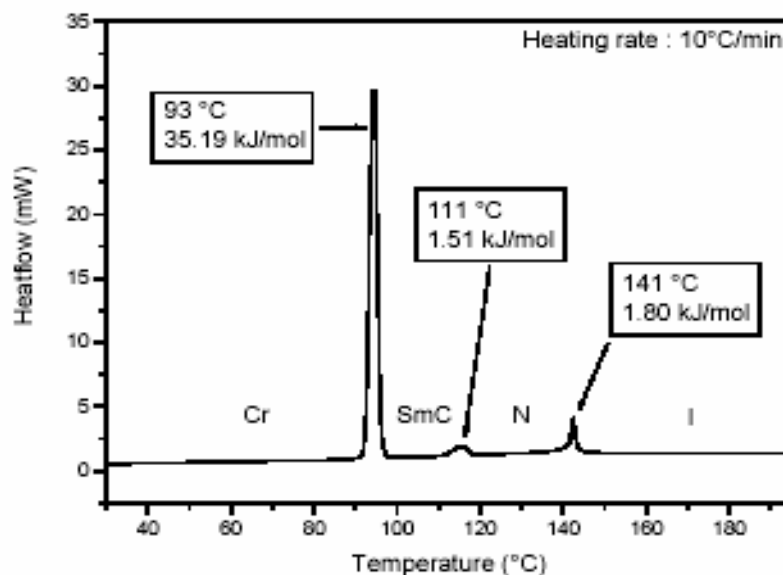


Figure 1.11 DSC thermogram of 4-nonyloxybenzoic acid²

Typically enthalpy changes between successive liquid-crystalline phases or between a liquid-crystalline phase and an isotropic liquid (clearing enthalpy) are small and at around 1-10 kJ/mol, while transitions between a crystal and a liquid-crystalline phase (melting enthalpy) are strongly first order and often in the range 20-50 kJ/mol. Typically heating rates are 10°C/min. DSC provides information on enthalpy of phase transitions which cannot be obtained from POM. DSC cannot be used to identify mesophases as POM is used. Thus the two methods, DSC and POM are complimentary to each other for the characterization of liquid-crystalline materials.

1.3.3 X-Ray Diffraction (XRD)

X-ray diffraction is a very useful method of identifying liquid crystal phases and determining how the molecules pack together. X-rays interact with the electrons in a material and pick out any periodically repeating features of a structure. The X-ray technique is based on Bragg's law, which relates the angle of incidence of the X-ray beam θ with the X-ray wavelength λ and the distance d between two planes.

$$n\lambda = 2d\sin\theta \quad (1.1)$$

The diffraction pattern of all the phases (mesophases) gives a very small number of independent Bragg reflections plus considerable structured diffuse scattering due to the large amount of disorder always present in these phases. For a true crystal the diffraction pattern consists of infinitely sharp peaks. For an isotropic phase only a diffuse peak is observed. For a liquid-crystalline phase the diffraction pattern shows generally one peak that is broadened at the base. Thus the liquid

crystalline phase shows X-ray characteristics that are intermediate between those of a true crystal and of a true isotropic fluid.

1.4 Applications of Liquid Crystals

Liquid crystal technology has had a major effect in many areas of science and engineering, as well as device technology. Applications for this special kind of materials are still being discovered and continue to provide effective solutions to many different problems.

1.4.1 Liquid crystal displays

By far the most important application of liquid crystals is in display devices. Liquid crystal display devices (LCDs) are now used in a wide range of equipment and apparatus such as watches, calculators, portable colour televisions, lap-top computer screens, car, and ship and aircraft instrumentation.

Liquid crystal display devices offer excellent features that are not provided by other types of display. LCDs are of a flat-panel design and are of low power consumption (mW). They are small and compact and hence used in portable displays. Another important feature of LCDs is the fast switching speed (ms-ms). The most common LCD that is used for everyday items like watches and calculators is called the twisted nematic (TN) display. A liquid crystal cell consists of a layer of nematic mesophase liquid crystal material between two glass plates with grooves. The glass plates have to be covered by a conductive layer. The direction of the grooves of the two glass plates are at 90° to one another.

When the liquid crystal material comes into contact with the grooved surface of the glass plate, the molecules line up parallel along the grooves as shown in Figure 1.12a.

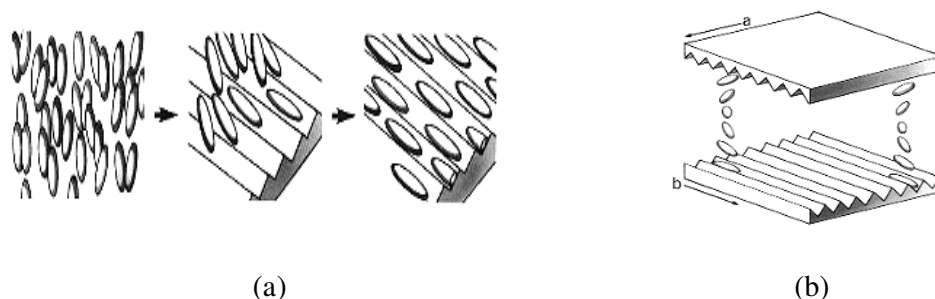


Figure 1.12 Molecules line up in (a) the grooved surface of the glass and (b) shows liquid crystal molecules in a twisted structural arrangement¹²

When liquid crystal material is sandwiched between the two glass plates, the molecules line-up with grooves pointing in directions 'a' and 'b' into a twisted structural arrangement as shown in Figure 1.12b. When light passes through the liquid crystal cells it follows the direction in which the molecules are arranged. When the molecule arrangement is twisted 90°, the light also twists 90° as it passes through the liquid crystals.

The molecules in liquid crystals are easily rearranged by applying voltage or another external force. When voltage is applied, molecules rearrange themselves vertically and light passes straight through along the arrangement of molecules. When voltage is applied to a combination of two polarizing filters and twisted liquid crystal, it becomes a liquid crystal display (LCD). The principle of twisted nematic liquid crystal display is shown in Figure 1.13.

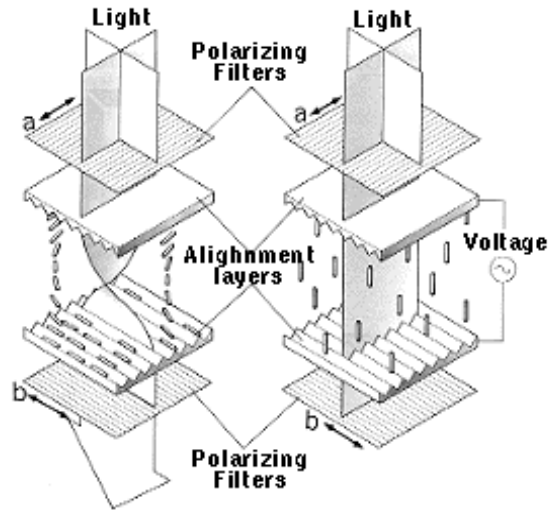


Figure 1.13 Principle of twisted nematic Liquid crystal displays (LCDs)¹²

When two polarizing filters are arranged along perpendicular polarizing axes, light entering from above is redirected 90° along the helix arrangement of liquid crystal molecules so that it passes through the lower filter. When voltage is applied, the liquid crystal molecules straighten out of their helix pattern and stop redirecting the angle of the light, thereby preventing light from passing through the lower filter and the entire device appears dark. In this way, applying voltage can be used to make a pixel switch between clear or dark on command. Colour LCD systems use the same technique, with coloured filters used to generate red, green, and blue pixels.

One of the advantages of liquid crystal displays is its ease of viewing. Flat panel TV displays like LCDs and Plasmas are significantly brighter and feature higher contrasts than traditional cathode-ray tube (CRT) sets. An LCD television will perform exceedingly well under ambient light conditions. TV can be watched

almost anywhere in a room since flat-screen LCD television displays can have up to a 160° viewing angle.

1.4.2 Liquid crystal thermometers

Certain liquid crystals reflect light with a wavelength equal to the pitch (the spacing between layers of similar orientation) and the reflected light will appear coloured. As the temperature of the liquid crystal changes, the spacing between layers also changes. The change in spacing changes the wavelength of the reflected light and its observed colour. Thus liquid crystals make it possible to accurately gauge temperature just by looking at the colour of the thermometer. By mixing different compounds, a device for practically any temperature range can be built. Special liquid crystal devices can be attached to the skin to show a “map” of temperatures. This is useful in finding tumors, because it has a different temperature than the surrounding tissue. Liquid crystal temperature sensors can be used to find bad connections on a circuit board by detecting the characteristic higher temperature.

1.4.3 Optical imaging

In this technology, a liquid crystal cell is placed between two layers of a photoconductor. Light is applied to the photoconductor, which increases the material's conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This

technology is still being developed and is one of the most promising areas of liquid crystal research.

1.4.4 Other Liquid crystal applications

Liquid crystals have a multitude of other uses¹³. They are used for nondestructive mechanical testing of materials under stress. This technique is also used for the visualization of RF (radio frequency) waves in waveguides. They are used in medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured. Low molar mass (LMM) liquid crystals have applications including erasable optical disks, full colour “electronic slides” for computer-aided drawing (CAD), and light modulators for colour electronic imaging.

1.5 Metallomesogens

Metallomesogens are transition metal complexes with ligands that exhibit liquid-crystalline character¹⁴. Metal containing compounds that exhibit mesomorphism can be either organometallic or classical inorganic coordination complexes¹⁵. Currently there is much interest in the synthesis and characterization of liquid-crystalline materials containing metal atoms because of the potential to modify many physical properties *via* the inclusion of a metal centre¹⁷. The introduction of an electron-dense metal centre should influence properties such as birefringence and dielectric anisotropy. The scope for these metallomesogens is great, since metals show a remarkable variety of geometries in addition to the linear, trigonal or tetrahedral arrangements exhibited by carbon. Since every metal atom features

large and polarizable electron density and many have unpaired electrons and are deeply coloured, the inclusion of metals opens up possibilities of new physical properties for the liquid crystals. Liquid-crystalline materials containing transition metals are attracting special attention because of the ability of the transition metal centre to impart unique optical, magnetic and electrical properties¹⁷.

1.5.1 Early Work on Metallomesogens

Vorlander reported the first thermotropic metal-containing liquid crystal in 1910¹⁸. He discovered that the alkali-metal carboxylates, $R(\text{CH}_2)_n\text{C}(\text{O})\text{ONa}$, formed classical lamellar phases characteristic of soaps. Later, in 1923, he also found that the diarylmercury Schiff bases $(\text{RC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4)_2\text{Hg}$ form smectic phases¹⁹. Other alkali and alkaline earth salts of carboxylic acids with organized mesophases were characterized by Skoulios and his collaborators²⁰, while the smectic ferrocenyl Schiff bases were synthesized by Malthete and Billard in 1976²¹. Giroud and Muller-Westerhoff reported the mesogenic nickel and platinum dithiolenes²² in 1977 and were the first to seek advanced materials (novel substances for electronic, optoelectronic and related applications) among such compounds.

This work laid the foundations for the study of mesogens containing d-block elements and marked the practical beginning of interest in the subject. Since then many new types of metallomesogens have been synthesized by using different varieties of ligands; monodentate (4-substituted pyridines²¹⁻²⁵, isonitriles²⁶, cyanobiphenyl derivatives²⁷), bidentate (salicylaldimine derivatives, β -diketonates, dialdehydes, aminoketones, dithiobenzoates, glioximates, alkanooates

etc.)²⁸⁻³⁷, or polydentate (phthalocyanines³⁸⁻⁴⁴, porphyrins⁴⁵⁻⁴⁷, triazine^{48,49}, triphenylene⁵⁰⁻⁵³).

Since mesophase formation depends on the intermolecular forces and the space around the metal occupied by the ligand, the properties of metallomesogens are dominated by the ligands and their arrangement, in other words by the overall shape of the molecule. Thus, for example, long monodentate ligands or bidentate ones with small bite angles will tend to give rod-like nematics and smectics, while flat space-filling polydentate ligands (for example macrocycles) will give discotic materials.

Another type of metallomesogens is metal-containing ionic liquid crystals. Ionic liquid crystals are ionic compounds, having liquid crystalline properties with low melting points (below 100°C). The groups of Bruce⁵⁴ and Seddon⁵⁵ reported results of metal-containing liquid crystals based on imidazolium salts which can also be classified as organometallic liquid crystals because of the metal-carbon bonds. A typical example of this type is given below.

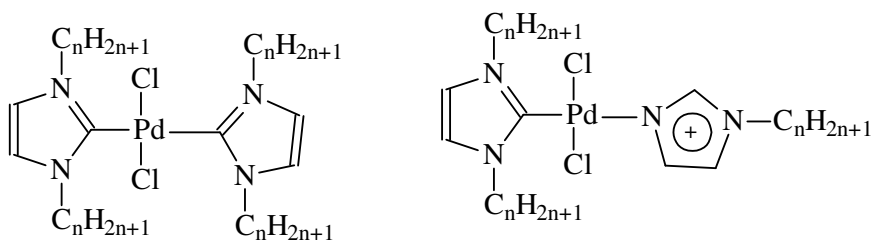


Figure 1.14 Metal containing liquid crystals based on imidazolium salts

The thermal stability of these compounds depends on the chain length; the longer the chain, the more stable the compound. The ordered environment and the unique structural properties possessed by metal-containing ionic liquid crystals can benefit the formation of nanomaterials with specific structure.

Recently Bruce and co-workers^{56,57} reported that the mesomorphism can change from the typical calamitic materials to discotic mesogens, simply by varying the chain length. Tetracatenar mesogens of the type shown below were used.

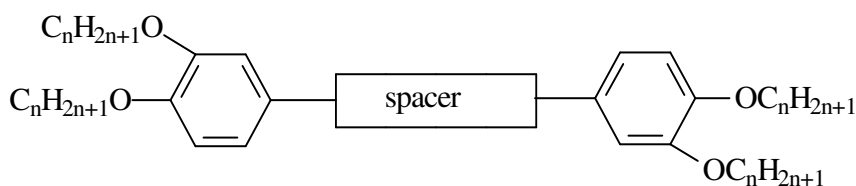


Figure 1.15 Tetracatenar mesogens

The compounds were constructed from long, rod-like cores that possessed four terminal chains arranged symmetrically. For short chain lengths the compounds displayed nematic and/or smectic C phases, while for longer chain lengths, they showed columnar phases.

1.5.2 Structural design of calamitic metallomesogens

The rod-shaped calamitic metallomesogens contain rigid central cores, with metal and the ligating atoms consist of ring structure phenyl or heterocycles, while flexible *n*-alkyl or -alkyloxy tails extend out along the molecular axes. The resulting rod-like polarizable core, together with the flexible end chains increase the molecular anisotropy and facilitate liquid crystal features¹⁷.

The magnitudes of the weak dipole-dipole and dispersion forces, which hold thermotropics together are critical: when they are too weak or when they are too strong, the liquid crystalline character is lost. Hence the molecular features, which optimize thermotropic behaviour, are very important.

1.6 Thiophene as building block

Thiophenes are aromatic compounds that display properties close to those of arenes. The thiophene molecule, C_4H_4S (Figure 1.16), is a five-membered, electron excessive heterocycle with excellent charge transfer properties. Thiophene has occupied an important position, firstly, because of its stability and secondly because of the versatility of the thiophene moiety in lending itself to synthetic modification.

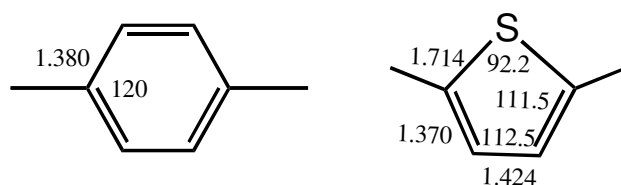


Figure 1.16 Structural properties of phenylene⁵⁸ vs thiophene⁵⁹ units

When comparing 1,4-disubstituted benzene units in chain structures, thiophene can change the polarity, polarizability and also the geometry of the compounds. This will alter the types of mesophases, phase transition temperatures, dielectric constants and other properties of mesogens. Thiophene systems generally have lower melting points because of poorer efficient packing in the solid state. The molecules have strong lateral dipoles with negative dielectric anisotropy and do

not require additional substituents such as F, CN, etc. to enhance these features. Additional substituents increase the breadth of the rod and can alter the viscosity of the system. Whereas 1,4-phenylene units promote linear structures, thiophene causes kinks or small bends in the chain. Because of these features thiophene-containing organic liquid crystals have been investigated extensively,⁶⁰⁻⁶⁴ but as part of metallomesogens have greatly been neglected and we are not aware of any examples. In addition, five-membered heterocycles such as thiophene and pyrrole have widely been used as building blocks for the design of well-defined linear π -conjugated oligomers and polymers⁶⁵. Conducting polymers based on thiophene and/or pyrrole have been reported to be soluble, and exhibit ordered crystalline or side chain liquid crystal phases⁶⁶. Crystallinity or liquid crystallinity in these materials can provide not only an insight into the electronic conductivity, but is also expected to lead to new applications that exploit anisotropic behaviour associated with the discrete, orthogonal conductivity mechanisms along the conjugated strands of the polymer material and between adjacent strands. In addition to this, the anisotropic properties associated with the liquid crystal phases might be manipulated or switched through some external stimulus. Although significant progress has been made in the synthesis of soluble/processible polymer systems, very few examples of conducting polymer systems that exhibit liquid crystal phases have been reported⁶⁰.

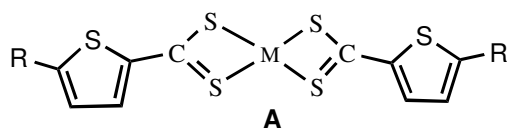
1.7 Dithiocarboxylate ligands

The dithiocarboxylate ligand, RCS_2 , is a strong bidentate chelating ligand with donor sulfur atoms. RCS_2 is considerably stable in complexes (all melt without

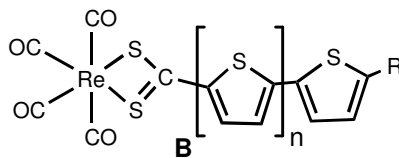
decomposition) contrary to the low chemical stability of the free ligands⁶⁷. Reactions of dithiocarboxylates and derivatives were extensively studied in the period 1967-1975 resulting in some fascinating chemistry and new structurally interesting complexes⁶⁸⁻⁷⁰. Many structural types with different modes of coordination of dithiocarboxylate ligands with metals have been documented. These include four-membered chelate rings, bridging dithiocarboxylate ligands and sulfur inserted perthiocarboxylate ligands. Complexes with dithiocarboxylate ligands displaying liquid crystalline properties have been reported for Ni, Zn, Pd and Pt transition metals^{33,71}.

1.8 Aim of study

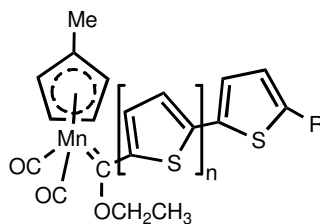
The main objective of this study was to synthesize metal complexes with ligands containing alkyl thiophene units in rod-like structures. The focus of the study was to find out the effect of the structural features of the new complexes and also to investigate their thermal properties. Dithiocarboxylate complexes of nickel(II) and zinc(II) with alkyl or alkyloxy substituted phenyl ring are reported to be mesomorphic^{22,33,72-77} whereas there are no known dithiocarboxylate complexes of nickel(II) or zinc(II) with alkyl or alkyloxy substituted thiophene. Figure 1.17 shows the alkylthiophene dithiocarboxylate complexes of Ni(II) and Zn(II). Another feature of interest is the electronic properties of thiophene adjacent to the coordinating CS₂ and the length of the alkyl chain.



M = Ni, Zn; R = H, alkyl



n = 0,1; R = alkyl



n = 0,1; R = alkyl

Figure 1.17 Target complexes with thiophene-containing ligands

The first chapter gives an overview of liquid crystals, their applications, early work on metallomesogens and structural design of calamitic metallomesogens. In the first part of the study, the synthesis, characterization, structural features and the liquid crystalline properties of the new complexes of nickel(II) with 5-alkyl-2-thiophenedithiocarboxylate ligands are investigated. The synthesis of the alkyl thiophene dithiocarboxylate ligands make use of known procedures adapted from dithiobenzoate⁷¹ synthesis and is modified to accommodate thiophene chemistry. Due to the diversity of the coordination modes recorded for dithiocarboxylate ligands with nickel(II), a careful assessment of the molecular structures was required. It is anticipated that the thiophene could play a major role in determining coordination modes as it is in direct π -contact via the coordinating CS₂ moiety

with the metal. The same ligands used for nickel were also used for zinc(II) complexes (Figure 1.17A). The nickel(II) complexes are d^8 systems whereas the zinc(II) complexes are d^{10} and both could give tetrahedral complexes. A comparison of coordination properties, the structural features and melting point behaviour of the new complexes were studied. In the second part of the study potential rod-like liquid crystalline properties of organometallic compounds were investigated. Two different types of complexes of group VII transition metals were selected, both containing carbonyl ligands. Firstly, the same dithiocarboxylate ligands were reacted as before to give $[\text{Re}(\text{CO})_4(\text{S}_2\text{CTR})]$ (Figure 1.17B) and this work was extended to include bithiophene. Bithiophene will lead to a greater polarization in the chain compared to thiophene. A weak point in this design is the many labile carbonyl ligands present in the complexes. However, luminescent rhenium(I) tricarbonyl complexes with long alkyl chains as spacers and terminal cyanobiphenyl groups displayed various mesophases⁷⁸. Carbene ligands of the Fischer-type will also display strong polarization effects because of the very electron positive carbene-carbon atom coordinated to the metal. This effect is studied again by including bithiophene in the ligand. Until now, no carbene complexes displaying mesophases have been studied. To prevent mass loss by carbonyl elimination under thermal condition the very stable $\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2$ metal fragment was selected⁷⁹ (Figure 1.17C). The rod-like structure is induced by attaching alkyl chains to the carbene ligand. The carbene complexes are expected to have low melting points because of the substituted cyclopentadienyl ($[\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_3]$ is an oil) ligand and are of interest to study.

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