Phases of liquid crystals

Introduction to Liquid Crystals

A liquid crystal is a thermodynamic stable phase characterized by anisotropy of properties Without the existence of a three-dimensional crystal lattice, generally lying in the temperature Range between the solid and isotropic liquid phase, hence the term mesophase. Liquid crystal materials are unique in their properties and uses. As research into this field Continues and as new applications are developed, liquid crystals will play an important role in Modern technology. This tutorial provides an introduction to the science and applications of these materials.

The term liquid crystal signifies a state of aggregation that is intermediate between the crystalline solid and the amorphous liquid. As a rule a substance in this state is strongly anisotropic some of its properties and yet exhibits a certain degree of fluidity, which in some case may be comparable to that of an ordinary liquid. The first observations of liquid crystalline or mesomorphic behaviour were made towards the end of the last century by reinitzer and lehmann.

What are Liquid Crystals?

Liquid crystal materials generally have several common characteristics. Among these are a rodlike molecular structure, rigidness of the long axis, and strong dipole and/or easily polarizable substituents. A dipole is present when we have two equal electric or magnetic charges of opposite sign, separated by a small distance. In the electric case, the dipole moment is given by the product of one charge and the distance of separation. Applies to charge and current distributions as well. In the electric case, a displacement of charge distribution produces a dipole moment, as in a molecule.

The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director (the molecular direction of preferred orientation in liquid crystalline mesophases). This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state. Note the average alignment of the molecules for each phase in the following diagram.

A mesogen is rigid rodlike or disclike molecules which are components of liquid crystalline materials. It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state. Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic (Having properties that are the same regardless of the direction of measurement. In the isotropic state, all directions are indistinguishable from each other)liquid has no orientational order. Substances that aren't as ordered as a solid, yet have some degree of alignment are properly called liquid crystals.

Liquid Crystal Phases

- Liquid crystal phases are formed by a wide variety of molecules.
- They can be divided into two classes, thermo tropic and allotropic. Transitions to thermotropic phases are initiated by changes in temperature, while those to lyotropic phases can also be initiated by changes in concentration.

Thermotropic Phases

- Thermotropic liquid crystals can generally be formed by prolate (calamitic) molecules or oblate (discotic) molecules.
- Liquid crystal phases formed by calamitic molecules fall into three different categories: nematic, chiral nematic, and smectic.

Nematic Liquid Crystal Phase

- The simplest liquid crystal phase is called the nematic phase (N). It is characterized by a high degree of long range orientational order but no translational order. Molecules in a nematic phase spontaneously order with their (for calamitic molecules) long axes roughly parallel. Schematic diagram of a nematic liquid crystal
- A uniformly aligned nematic has a preferred direction, often described in terms of a unit vector called the director. More generally a bulk nematic will contain domains. The orientation of the director is constant in each domain but is different in different domains. Viewed under a polarizing microscope the defect regions linking these domains appear as dark threads

Chiral Nematic Liquid Crystal Phase

- Chiral molecules can also form nematic phases called chiral nematic (or cholesteric) phases (N*). This phase shows nematic ordering but the preferred direction rotates throughout the sample. The axis of this rotation is normal to the director.
- An example of this is shown in Fig (b). The distance over which the director rotates by 360 is called the chiral pitch and is generally of the order of hundreds of nanometres, the wavelength of visible light. A

non-chiral nematic phase can be thought of as a chiral nematic with an infinite pitch. Fig (b).

Smectic Liquid Crystal Phases

Smectic phases have further degrees of order compared to the nematic phase. In the simplest smectic phase, the smectic-A (SmA) phase, the molecules order into layers, with the layer normal parallel to the director. Within the layers, liquid like structure remains, as shown in Fig. 1. 3.

Closely related to the SmA phase is the smectic-C (SmC) phase. Here the molecules form a layer structure but the long axes of the molecules, and hence the director, lies at an angle to the layer normal, as shown in Fig. 1. 4. There are many other smectic phases which have long range order within the layers Smectic phases can also be formed by chiral molecules, leading to chiral smectic phases.

Discotic Liquid Crystal Phases

- Liquid crystal phases formed by discotic molecules fall into three different categories: discotic nematic, discotic chiral nematic, and columnar.
- The discotic nematic is similar in structure to the calamitic nematic, although in this case the short axes of the molecules tend to lie parallel. The same holds for the discotic chiral nematic phases.
- Columnar phases are the discotic equivalent of the smectic phase. Here the molecules form columns. In the simplest case the short axes of the molecules lie parallel to the axis of the column and the columns are randomly distributed in space. More complicated discotic phases exist, where the short molecular axes lie at an angle to the column and

translational order exists between the columns, analogous to the more complicated smectic phases.

Other Thermotropic Phases

Most of the phases exhibited by low molecular mass liquid crystals are described above. Recently however there has been much interest in the so-called `banana’ phases formed by bent-core molecules

- Some of these phases are chiral although the molecules forming them are achiral.
- Some high molecular mass polymers, liquid crystalline polymers (LCP), can also form liquid crystal phases.
- These fall into two categories depending on where the mesogenic part of the molecule is located. If the mesogenic unit is contained within the main polymer chain then it is termed a main chain liquid crystal polymer (MCLCP).
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Lyotropic Liquid Crystal Phases

- Lyotropic liquid crystal phases are formed by amphiphilic molecules.
- These often consist of a polar head group attached to one or more non-polar chains and are often known as surfactants (surface active agents).
- A schematic is shown in Fig. 1. 5. When these are dissolved in an appropriate solvent they self-assemble so the polar (hydrophilic) heads

protect the non-polar (hydrophobic) tails. These structures are known as micelles.

- At low surfactant concentrations these are roughly spherical, as shown in Fig. 1. 6. As the surfactant Concentration increases then other phases are formed.
- These include the hexagonal phase where the amphiphiles form cylinders that pack in a hexagonal array and the lamellar phase where the amphiphiles form a bilayer structure.

Structure-Property Relationships in Liquid Crystals

- Despite this there exists only a poor understanding of how changes in molecular structure affect material properties. For liquid crystals this is complicated by several factors.
- Firstly, liquid crystal phases are formed by materials from the whole spectrum of chemical classes: organic, organometallic, and biological molecules can all form liquid crystal phases.
- Secondly, mesogenic molecules are generally quite large. A typical low mass mesogen will have from about 40-100 atoms. For liquid crystalline polymers and dendrimers this can be closer to a few thousand atoms. Liquid crystals tend to be flexible. This inhibits crystallization, preventing the direct transition from an isotropic liquid to a crystalline solid. It also leads to a large degree of conformational freedom, so properties are generally determined by more than just the equilibrium structure.

- Finally liquid crystal molecules often contain disparate parts (such as alkyl and perfluoroalkyl chains) that can have a large effect on the phase behaviour.
- Investigation of these factors by experimental or theoretical means should hopefully lead to a better understanding of structure-property relationships in liquid crystals.
- In principle the relationship between molecular structure and macroscopic properties can be investigated through the synthesis of series of similar mesogenic compounds. This however can be time consuming and may involve many difficult and expensive syntheses. Thus, the ability to determine the properties of a molecular structure before synthesis would be desirable. It is here that simulations can play an important role. Simulations on general molecular models can be used to find features that can lead to a particular property or phase.
- Atomistic simulations can be used to determine material properties of a particular molecular structure.

Chemical Properties of Liquid Crystals

Liquid crystals can be classified into two main categories: thermotropic liquid crystals, And lyotropic liquid crystals. These two types of liquid crystals are distinguished by the mechanisms that drive their self-organization, but they are also similar in many ways. Thermotropic transactions occur in most liquid crystals, and they are defined by the fact that the transitions to the liquid crystalline state are induced thermally. That is, one can arrive at the Liquid crystalline state by raising the temperature of a solid and/or lowering the temperature of a Liquid.

Thermotropic liquid crystals can be classified into two types: enantiotropic liquid crystals, Which can be changed into the liquid crystal state from either lowering the temperature of a Liquid or raising of the temperature of a solid, and monotropic liquid crystals, which can only be Changed into the liquid crystal state from either an increase in the temperature of a solid or a Decrease in the temperature of a liquid, but not both. In general, thermotropic mesophases occur Because of anisotropic dispersion forces between the molecules and because of packing Interactions.

In contrast to thermotropic mesophases, lyotropic liquid crystal transitions occur with the Influence of solvents, not by a change in temperature. Lyotropic mesophases occur as a result of Solvent-induced aggregation of the constituent mesogens into micellar structures. Lyotropic mesogens are typically amphiphilic, meaning that they are composed of both lyophilic (solventattracting) And lyophobic (solvent-repelling) parts. This causes them to form into micellar structures in the presence of a solvent, since the lyophobic ends will stay together as the lyophilic ends extend outward toward the solution. As the concentration of the solution is increased and The solution is cooled, the micelles increase in size and eventually coalesce. This separates the newly formed liquid crystalline state from the solvent.

A very large number of chemical compounds are known to exhibit one or several liquid crystalline phases. Despite significant differences in chemical composition, these molecules have some common features in chemical and physical properties. There are two types of thermotropic liquid crystals: discotics and rod-shaped molecules. Discotics are flat disc-like molecules consisting of a core of adjacent aromatic rings. This allows for two dimensional columnar ordering. Rod-shaped molecules have an elongated, anisotropic geometry which allows for preferential alignment along one spatial direction. The rod-like low molar mass (LMM) liquid crystals, such as 5CB shown in the following Diagram: require an extended conformation of the molecule which must be maintained through the rigidityand linearity of its constituents. That is, in order for a molecule to display the characteristics of a liquid crystal, it must be rigid and rod-shaped. This is accomplished by the interconnection of two rigid cyclic units. The interconnecting group should cause the resulting compound to have a linear planar conformation. Linking units containing multiple bonds such as -(CH= N)-, -N= N-, -(CH= CH)n-, -CH= N-N= CH-, etc. are used since they restrict the freedom of rotation. These groups can conjugate with phenylene rings, enhancing the anisotropic polarizability. This increases the molecular length and maintains the rigidity.

Applications of Liquid Crystals

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

Liquid Crystal Displays

The most common application of liquid crystal technology is liquid crystal displays (LCDs.) This Field has grown into a multi-billion dollar industry, and many significant scientific and Engineering discoveries have been made.

Liquid Crystal Thermometers

As demonstrated earlier, chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch. Because the pitch is dependent upon temperature, the color reflected also is dependent upon temperature. Liquid crystals make it possible to accurately gauge temperature just by looking at the color of the thermometer. By mixing different compounds, a device for practically any temperature range can be built. The “ mood ring”, a popular novelty a few years ago, took advantage of the unique ability of the chiral nematic liquid crystal. More important and practical applications have been developed in such diverse areas as medicine and electronics. Special liquid crystal devices can be attached to the skin to show a “ map” of temperatures. This is useful because often physical problems, such as tumors, have a different temperature than the surrounding tissue. Liquid crystal temperature sensors can also be used to find bad connections on a circuit board by detecting the characteristic higher temperature

Optical Imaging

An application of liquid crystals that is only now being explored is optical imaging and recording. In this technology, a liquid crystal cell is placed between two layers of photo conductor. 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.

Other Liquid Crystal Applications

Liquid crystals have a multitude of other uses. 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 color " electronic slides" for computer-aided drawing (CAD), and light modulators for color electronic imaging. As new properties and types of liquid crystals are investigated and researched, these materials are sure to gain increasing importance in industrial and scientific applications.