LIQUID CRYSTAL PHASES
http://liqcryst.chemie.uni-hamburg.de/lcionline/liqcryst/lcintro/lcframe.htm
University of HAMBURG

Introduction

Matter in nature is a collection of large number of atoms and molecules interacting under well defined forces. Matter can exist in many different stable states called phases. The simplest atom helium can be found in gaseous, liquid and solid states under different thermodynamic conditions. How the matter consisted of the same atom differ in different states?

In gaseous state, the particles are randomly distributed in free space. There is no correlation between the particles that move in independent trajectories bouncing off of each other. The gases can not be seen because average distance between particles is larger than the wave length of visible light. In liquids, the particles are also distributed randomly in space but with specific correlation among them. In crystalline solids, on the other hand, particles are located in fixed positions relative to each other. Furthermore, the locations are arranged in periodic arrays called lattice. They can be visually observed because the distance between the particles are much shorter than the wave lengths of visible light.

The basic difference among sates of matter is that the constituent particles are arranged in different geometrical configurations under different thermodynamic conditions. In general, for a given external conditions such as temperature, pressure, volume etc., specific molecular interactions determine the possible configurations of the given system.

In a crystalline solids, particles are orderly stacked in a lattice which is symmetric only under a discreet set of translations and rotations. Certain physical properties observed in asymmetric directions may differ. So, crystalline solid state has low symmetry and is anisotropic and ordered.

In a physical system of gaseous and liquids, finding a particle at any point in space is independent of the position and the direction. There is no way to tell how to find a particle at a position with respect to another particle. The constituent particles are distributed in a geometrically symmetric configuration. Its physical properties are independent of the direction of observation. So gaseous and liquid states commonly called fluid state, in contrast to crystalline solid state, have full translational and rotational symmetry and are isotropic and disordered.

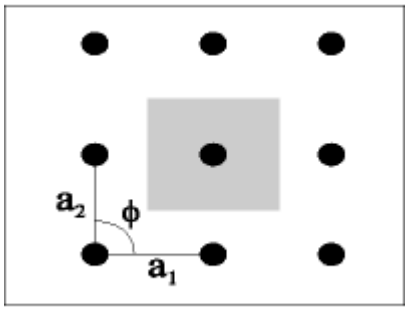


FIGURE 1

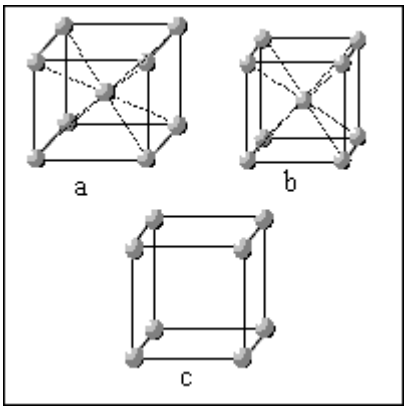


FIGURE 2

A symmetry operation of physical system is a geometrical transformations of its constituent particles in three dimensional space leaving the equilibrium state of the system unchanged. Symmetry operations are consisted of rotations, reflections, and inversions about an special symmetry points and directions. The fundamental distinction between different states is their symmetry. A physical system can transform from a state with full symmetry into a state with lowest symmetry under different thermodynamic conditions. A physical system can also exist in a state intermediate between highest symmetry fluid and lowest symmetry crystals. In this case, symmetry can exist only in one or two dimension. Intermediate states have short range order in some directions and long-range order in other directions. One form of the order in intermediate states is their orientational order. These intermediate states can have flow properties of isotropic liquids, and anisotropic properties of crystalline solids. They can solidify into crystals at low enough temperatures and melt into liquid at higher temperatures. The liquid crystals belong to systems show this intermediate order. Liquid crystalline phases are also known as "mesophases"

Molecular Structure

The same phase can be formed by molecules which are widely varies in their structure and molecules with same structure can form variety of phases. All the parameters which determines what phase a molecule with known structure will form are not known. But the structure of the molecules and the phases those molecules form are very closely related.

Liquid crystalline phases are formed by many different type of molecules which differ widely in their structure. Even though the shape of the molecules are complicated, often they are referred to as rod like or disk like. For instant, shape of a molecule with several benzene rings aligned in different angles is quite far from being a rod. But the simplifications is appropriate because a phases with similar macroscopic properties can result from molecules with diverse chemical structure. If the length is considerable larger than the width, only detail of molecular structure that is important is the ratio of length to width. For an example, optical characteristics of liquid crystals in electric or magnetic field suggest that the real shape of the molecules does not give rise to observable effect.

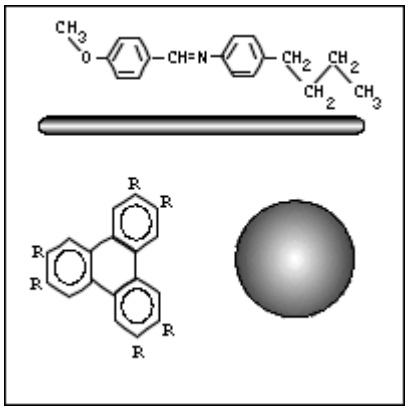


FIGURE 3

All the known molecules that form liquid crystalline phases are asymmetric in their shape. Some of them are long , rigid and rod like. Some of them are flat and disk like. Another group of molecules which form liquid crystal phases are lath like which does not have cylindrical symmetry. These systems can have one or more liquid crystalline phases.

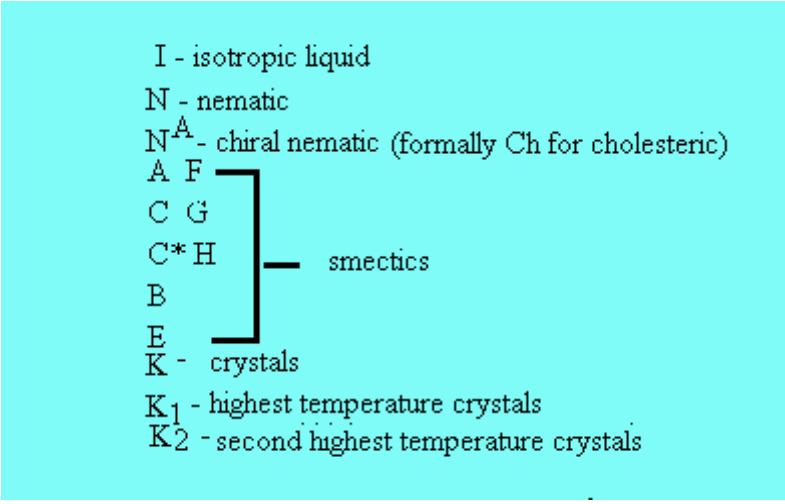
The molecules which does not have mirror symmetry are called chiral. They can form mesophases with modulated helical structures. The chiral molecules also can be added to modify the properties of existing mesophases.

FIGURE 4

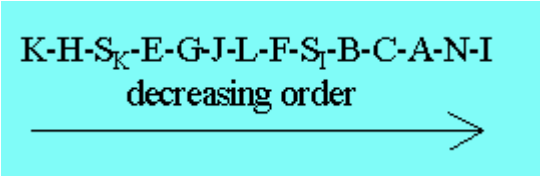
Polymers are typically consisted of very large molecules, molecular weight of 10,000, 100,000 or even greater which are made up of repeated units of smaller molecules called monomer. Monomer can be attached in a long single chain forming main chain polymer or can be attached to polymer back born forming side chain polymer. There are mesophases formed by polymeric molecules. They combine the unique properties of polymer such as high strength fiber or ultra thing films and anisotropic properties of liquid crystals.

Liquid Crystal Phases

During these characterization studies, mesophases were given various letter designations according to the order in which they were discovered. As long as only a few groups used this system, no assignment problems developed. However, with more researchers automatically assigning the next letter to what they felt was a new mesophase, problems developed. Identifications had to be changed to avoid confusion. For some phases, such as crystals, a wide variety of designations have been used (C, Cr, Crys, K, Kr). Additionally, there are different ways of indicating these letters for smectics: smectic A, S_A, SA or A. A group of scientists are now trying to develop a universal set of standard designations. For the discussion here, the following will be used:



The current classification system gives the following order of mesophases for those that are non-chiral:[274]



Known transitions between phases have been summarized [274,275] as well as the structures of these phases. [274,276a]

The order of these phases is very useful in identifying mesophases when polymorphism (more than one mesophase) occurs. For example, a Semitic B phase can occur below any of the phases C, A and N, but not below F. The only exception to this rule occurs in reentrance where a second nomadic phase can occur below a Semitic A phase or a second A below a reentrant nomadic phase. This can occur only in certain types of structures, all of which have a strong dipole along the molecular axis.

Thermotropics

Thermotropic liquid crystals are obtained by partial melting of solid crystals of certain materials. These systems are consisted of single components and most known substances are organic compounds. These materials are isotropic liquid at higher temperatures and crystalline solids ate lower temperatures. Liquid crystalline phase can be distinguished from isotropic liquid by its turbid appearance and from solid crystals from its flow properties.

The liquid crystal phases are also known as mesophases. The names of different liquid crystalline phase are due to G. Fiedel who studied many of their properties in early part of this century. There are two main liquid crystal phases. Nematic which has orientational order and no positional order. Smectic, which has orientational order and positional order only in one dimension, are formed in layered structure. There are several smectic phases (polymorphism). A given substance may have one or more mesophases. The sequence of the known phases are,

$$\text{Crystal} \Leftrightarrow S_I \Leftrightarrow S_G \Leftrightarrow S_F \Leftrightarrow S_B \Leftrightarrow S_C \Leftrightarrow S_A \Leftrightarrow N \Leftrightarrow I$$

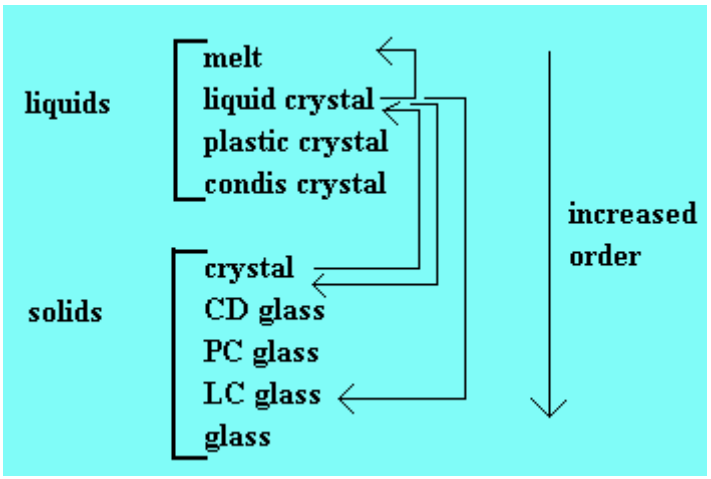
The liquid crystal molecules anisotropic, their length to with ratio is large and have rigid polarizable part. It is accepted that permanent dipoles are not very important for formation of mesophases. Orientation of the rod like molecules can be described by introducing two local axes, one parallel to the molecule known as long axis, and one perpendicular to it known as short axis. The molecules tend to align parallel to each other on the average leading to a preferred direction in space. The direction of this local alignment usually described by a unit vector $\hat{n}$ called director. There have been no evidence that indicates the polarity of the molecules has any effect on their phase behavior or physical properties. This leads to a conclusion that $\hat{n}$ and $-\hat{n}$ are equivalent.

There are several methods used to identify liquid crystalline phases. Differential Scanning Calorimetry (DCS) can be used to determine transition temperatures, therefore to distinguish phases. But one can not identify the phases itself by this method. Polarizing microscope is the most widely used method in identifying different phases. One can look at a thin layer of liquid crystal substances placed in between two glass cover plates. Depending on the boundary condition and the type of phase, varies textures which are characteristics of a phase are observed. Usually the textures change while going from one phase to the other. Polarizing microscopy is powerful too when used in combination with miscibility of binary mixtures. Most precise techniques in identifying phases and arrangements of molecules are X-ray and neutron scattering technique. These techniques provide direct information of the positional and orientationl characteristics of liquid crystals.

Characterization

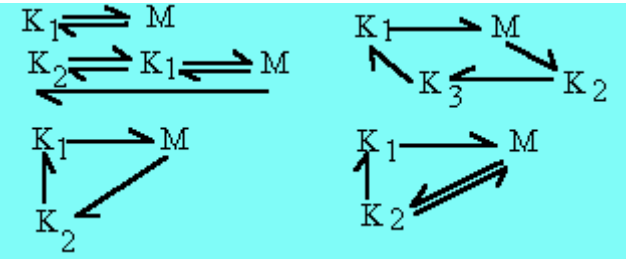
The initial determination of mesomorphic properties for a new compound are usually determined by the chemists who synthesized these materials. Two widely used methods that require relatively inexpensive equipment are hot-stage polarizing microscopy and thermal analysis via differential thermal analysis (DTA) or differential scanning calorimetry (DSC). A third method, usually requiring interaction with another scientist and more expensive equipment, is x-ray crystallography.[259-261] This method usually defines the structure of the phase and is used to confirm the identifications provided by the first two methods or to characterize a new mesophase. Phase transitions can further be studied by numerous additional methods, such as adiabatic calibration. Only the first two methods will be discussed here as they are the only ones normally employed by the synthesis chemist.

To be able to accurately determine mesomorphic properties, an understanding of the relationship between liquid crystals and other states of matter is needed. A summary of the relationships between solids and liquids can be found in the literature.[262] Those pertinent to the discussion here are as follows:



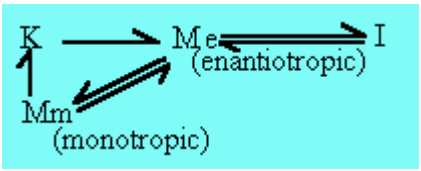
It is also quite common to observe crystal-to-crystal changes in materials designed to have mesomorphic properties. This is not surprising since designing such molecules requires achieving a delicate balance between flexibility and rigidity to allow for stepwise melting.

A variety of crystal-to-crystal changes are possible. They can occur on heating fresh (virgin) crystals before melting takes place or only on cooling. These crystals can convert to the virgin crystals or they might not within the time of a transition study. Of course this depends on how long a sample sets. Sometimes it will take awhile and reheating too soon may give a much broader melting transition than if allowed to set overnight. Different crystal forms can also show different melting temperatures. Up to three crystal forms are sometimes observed; more can rarely be detected. The following schematic diagrams show some of the various possibilities with the highest temperature crystals always being labeled K_1 and M=mesophase.



The phenomena of supercooling of fluids is also essential for accurately determining mesomorphic properties. Isotropic liquids usually supercool before they crystallize under non-equilibrium conditions. This is also true of mesophases. This means that the crystallization temperature will usually be less than the melting temperature. With some compounds, this supercooling will be small (~ 10) and therefore appear to be non-existent, but in most compounds it is large enough to be easily detected. In some compounds, it can be quite large. It tends to be larger in branched, chained mesogens than in straight chain ones. Since supercooling represents an unstable condition, it also means that the crystallization temperature is dependent on such things as cooling rate, vibration and previous history of the sample. Transitions between mesophases usually do not involve supercooling. Thus, supercooling can serve as a means for differentiating between crystals and mesophases. As is true in structure-property relationships, there can be exceptions, but these are rare. The first goal of determining mesomorphic properties should be to determine if the phase transitions that are observed involve mesophases rather than crystal phases.

The supercooling of fluids makes it possible to observe additional mesophases called monotropic phases. Such mesophases are not observed on heating from crystals, but can be seen on cooling a sample below the melting temperature. This transition is reversible as long as it occurs before crystallization. Thus, the best definition for monotropic phases is that they are mesophases that occur below the melting temperature and not that they are ones that occur only on cooling:



An enantiotropic mesophase is one that occurs above the melting temperature and is therefore seen on melting the sample from crystals (or a lower temperature mesophase) to the isotropic liquid lowest temperature mesophase and always seen on cooling with some compounds, a monotropic phase occurs slightly below the melting temperature within the experimental error of the temperature sensor of the measuring device. These are difficult to determine whether they are enantiotropic or monotropic, but carefully repeated results often makes this possible. Sometimes the mesophase ranges are so small that the best that can be done is to call the melting transition a K® M_{12} transition. For example, K-S_{BC}. This is also true of some mesophase transitions.

It is also possible to have two crystal forms, one of which melts to a mesophase on heating giving an enantiotropic mesophase, and another that does not melt to this mesophase but forms it on cooling giving a monotropic phase due to the fact that the two crystal forms have two different melting temperatures.

Microscopic Textures

The pioneering work of Arnold, Sackmann and Demus (a complete listing of their papers can be found in reference 263) characterized many mesogenic textures and developed a classification system from contact mixture studies and phase diagrams based on the rule that identical mesophases will be miscible in all proportions [264-266] The simplest method is the contact mixture study. A small sample of the new material is placed on one side of the viewing area of a slide. A known sample is placed nearby leaving a small gap between the two in the center. A cover slip is added, the slide inserted into a heating stage and heated until both samples melt to the mesophase being characterized. If the two mesophases are different, a boundary will occur in the center. This can be easily seen in

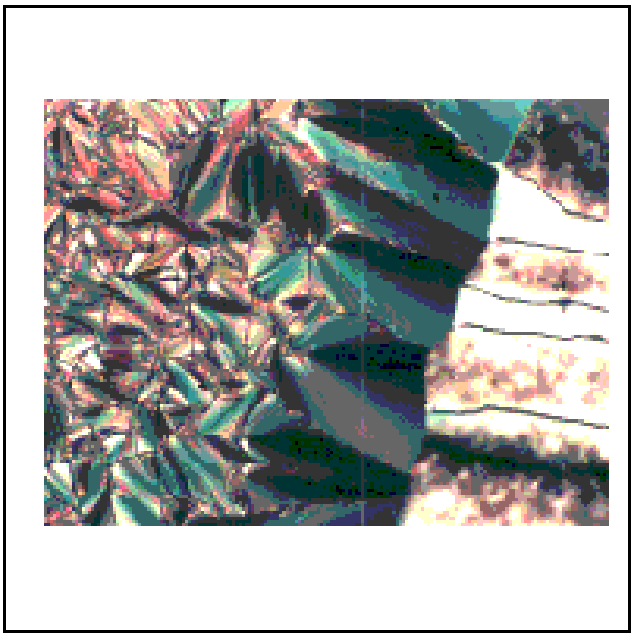


Figure 5

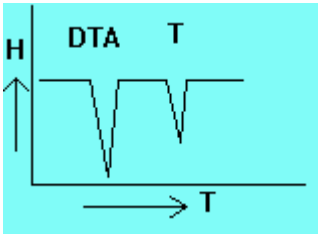
between the nematic and smectic A phase. However, it is smectic phases which usually need to be identified. although some boundaries between smectics are obvious, such as smectics A and C, others are more difficult such as smectics A and B. It can also be difficult to determine if a boundary exists between two smectic phases when both give mosaic textures. Another problem is that both mesophases must occur in approximately the same temperature range. Also, the two mesophases may seem to be miscible in all proportions in contact mixture studies, but actually show a small region of immiscibility in the more accurate phase diagram. A detailed phase diagram was needed to show that the phase in TBBA that was initially thought to be a biaxial smectic B phase was not a B but a smectic G phase. [264-267] Still, these two methods have been used extensively in conjunction with x-ray crystallography to characterize

smectic phases by type, their order in a sequence and to develop a classification system. [268] mesogenic series showing numerous smectic phases were particularly useful. These include the anils, [269,270] dianils, [271,261,270] pyrimidines [270] and biphenyl esters. [272] These studies were reviewed and the classification updated at successive International Liquid Crystal Conferences [264,273] until recently.

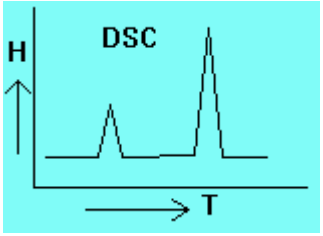
Thermal analysis

Another method for determining mesomorphic properties involves the use of thermal analysis equipment. Since heat is required to induce a phase transition between two phases having different levels of order, determining this heat can be a useful means for detecting phase transitions. Three types of calorimetric thermal analyses have been used in the liquid crystal area: classic adiabatic calorimetry (CAC), differential thermal analysis (DTA) and differential scanning calorimetry. Classic adiabatic calorimetry is the most precise and versatile method. It was the sole method used in early determinations of enthalpy values for liquid crystals [304] It is however a very time consuming method requiring expensive equipment and initially, requiring large quantities of material. Later modifications made it possible to use smaller samples [305,306] It is still used today to determine heat capacities or for more detailed studies of phase transitions. However, the development of DTA and DSC instruments made it possible to determine values faster, more conveniently and at a lower cost albeit less accurate. This method is now widely used to evaluate large numbers of new mesogens [307].

The difference between the DTA and DSC methods is simply in the way the heat of transition is measured and recorded. In DTA, this heat is measured directly so that in a heating scan, the peaks are negative:



whereas in DSC, heat is added to compensate for the heat absorbed so that the peaks are positive:



General thermal analysis reviews discuss equipment and techniques that are available [308, 309]. Several reviews discuss the early work done with liquid crystals [546, 579, 595]. DSC instruments seem to now be more popular than

DTA ones. Thus, this discussion will concentrate on the DSC method as another method for organic chemists to determine mesomorphic properties.

Since the enthalpy of phase transitions can be determined by DSC, this method provides information which cannot be obtained by microscopy. A comparison of phase transition data determined by DSC and microscopy has been made[313] Generally, DSC is poor at detecting low enthalpy transitions such as second order ones, but better for observing some crystal-to-crystal changes. DSC cannot be used to identify mesophases as microscopy can be. Thus, the two method complement each other. It is therefore not surprising that some instruments have been developed which combine both of these techniques [271, 314-316]. DSC has also been combined with x-ray diffraction equipment [317].

Other data can also be obtained from DSC scans. The entropy of transition can be obtained from the relationship of D H = T D S. Because of this relationship, discussions of enthalpy value trends also apply to entropy values. Other information obtained from DSC _____ include purity, [318-320] phase transition order, [321,322] conformational disorder [262] and molecular shapes, [323] although not all of these employ simple DSC scans.

Although small enthalpy transitions are difficult to observe, they can sometimes be observed by using larger samples, increasing the sensitivity or changing the heating rate. Small enthalpy transitions include the following: S_C-S_A, S_G-S_F, Ch-blue phase, and S_A-$S_{A\sim}$. There is no latent heat for the second order SC-SA transition, but there is a small enthalpy change due to the change in the tilt angle. [322] Sometimes this can be detected by using a sensity of and a heating rate of 5° /min [313].

Today, obtaining a DSC is relatively easy. The instrument must first be calibrated. This is usually done with indium since metals can often be obtained with a higher purity than organic materials. However, highly purified liquid crystals have also been used for calibration [324]. Then an accurately weighed sample is placed in an aluminum pan, crimped tightly closed with a sealing press and placed in the sample chamber of the DSC instrument. Instructions are provided with each type of instrument for obtaining a good DSC scan. Since the peaks are often not symmetrical, the center of a peak cannot be used as the transition temperature. The determination of transition [308] temperatures is discussed in the literature [325], but today's instrument is operated by a computer data station which determines both the transition temperature and the enthalpy of the transition. Determining D H values involves drawing the best base line [326]. Since mesophase transitions may involve pre or post transitional effect, second order transitions of small D H values, determining accurate D H values can be difficult [321] Accuracy tends to decrease with decreasing D H values [327] Before the use of computers for D H calculations, the error in D H values from author to author could be as much as 10%[311,310] However, a computerized TADS system on a DSC can give D H values in good agreement with CAC studies [325,327].

Once a good curve is obtained, then it must be accurately interpreted as a number of factors affect the peak shape and area. The first step should be to eliminate the possibility that a peak is due to a crystal-to-crystal change.

These changes as well as crystallization depend on both the cooling rate and the history of the sample as discussed earlier in the microscope section. Of course, the appearance of the DSC curve will be affected by these transitions. It is important to remember that due to supercooling, most melts will crystallize at a lower temperature than the solid melts. As with microscopy, this can be useful in differentiating crystal changes and crystallization from mesophases. The first peak that occurs in a cooling DSC scan below the melting temperature and is not immediately reversible is a crystallization peak. A reversible peak can be due either to a mesophase transition or a crystal-to-crystal change. Usually, the largest peak in both the heating and cooling curves are due to melting the solid and crystallization respectively. Smaller peaks below these are usually due to crystal-to-crystal changes. However, there are some exceptions to this. If the crystalline phase that melts to a mesophase has nearly the same order, then the D H of melting may be small. This sometimes occurs when melting takes place through a series of several crystal forms. The same thing is true of crystallization. Crystal changes may occur at the same temperature in both the heating and cooling curves or they might not. Mesophase transitions generally will occur at the same temperature, if the mesophase is reheated immediately.

Sometimes a mesogen can form two crystal forms that melt at two different temperatures. This also will produce a different DSC scan on reheating a cooled sample immediately. Some mesophases take a long time to crystallize. This is often true of smectic B phases that occur below smectic C phases. Such samples may have to set overnight before a second heating scan is done to obtain a melting curve. Some mesogens form glasses, another transition that occurs below the crystallization one.

In order to obtain as accurate and complete thermal history as possible by DSC, a good approach is to first heat the virgin crystals (usually obtained by recrystallization) at a rate of 10° /min until the sample converts to the isotropic liquid, cool until crystals form, reheat to the isotropic liquid, cool to room temperature (or below if necessary), allow the sample to remain at room temperature for a long time and then reheat. If a sample is reheated before crystals are obtained, this scan will look different than the original one since the melting peak will not be observed. Sometimes crystals are formed, but these slowly change to another form. Reheating this sample will give a different melting peak (often a broader one). Sometimes a crystal-to-crystal change can occur before the melting transition. This may be a true temperature change, but often it is simply a time effect. It is common to find that the D H from the melting of virgin crystals is larger than that of the crystallized melt. This is because sufficient time has not been allowed to obtain the D H of all the crystal changes. Thus, the most accurate value for the D H of melting is that obtained from a virgin sample. This is why Merck has chosen this melting D H as the one for evaluating their compounds [307] Examples of DSC curves of several types of crystal changes can be found in the literature [328].

Typical DSC scans which illustrate many of these points are given in

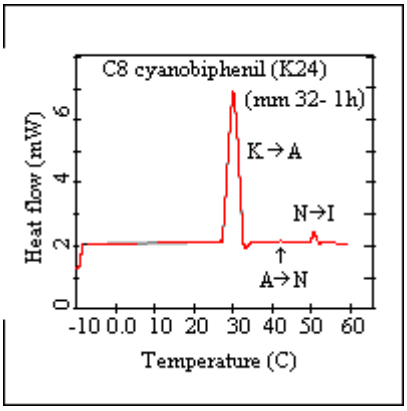


FIGURE 6

Transition temperatures for these mesogens can be found in Table XV. In

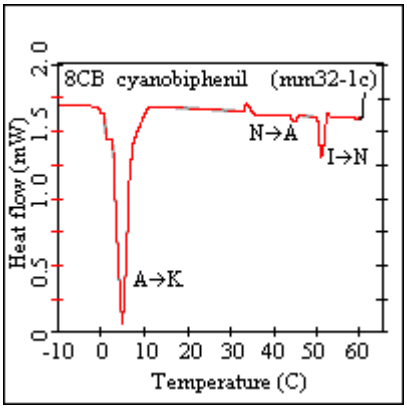


FIGURE 7

the A-N transition is barely detectable; it is likely this transition would be missed using DSC scans only. A good example of the complexity of solid transitions found in melting in crystallization can be seen in

FIGURE 8

Three crystal forms were observed both in the microscopy and DSC scans, but these vary according to sample history.

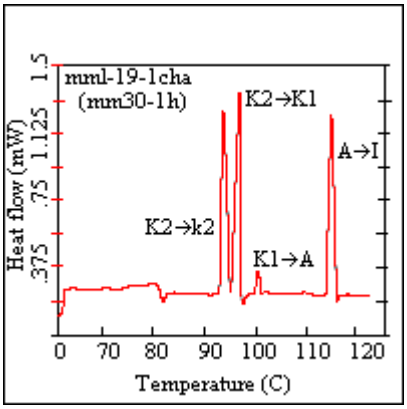


FIGURE 9

shows the supercooling effect that confirms that all of these phases are crystals and not mesophases.

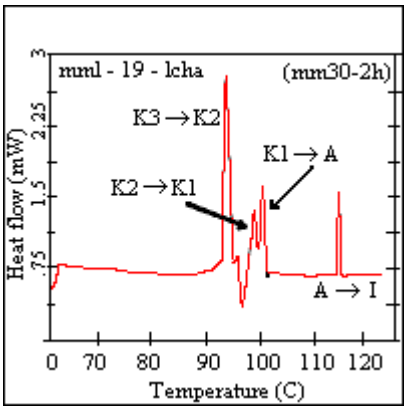


FIGURE 10

shows the low D H transitions for the more highly ordered smectic phases in TBBA. Note that in this normal scan the C-A transition is not detected.

TBBA illustrates both monotropic and enantiotropic smectic phases, C-A transition not detected in this normal scan, crystallization (55.6°) occurs below the melting temperature (112.9°) as do the monotropic mesophases. No crystal changes observed. Peaks for crystallization and melting have the largest D H values. D H crystallization is less than D H melting.

Relationships between molecular structures and enthalpy values have been studied just as the relationship between structure and transition temperatures have. Various homologous series have been studied such as anils, [270] dianils, [329,303,267,270] cyclohexane diesters, [330]. cholesteryl esters, [310,311] azoxy compounds, [310] and pyrimidines [331,270]. However, a lot of enthalpy data have been collected for the use in eutectic composition calculations. All of these data are now available in some of the databases previously discussed. Three factors need to be considered in comparing enthalpy values either within a homologous series or for different structures. Data coming from a variety of sources can show a large error variation. Secondly, different types of melting or clearing transitions will have different values. For example, the enthalpy for crystal to smectic B should be smaller than crystal to isotropic liquid. Thirdly, the enthalpies of all crystal changes must be included in the enthalpy of melting. Even so, enthalpies of melting can change throughout a homologous series simply because melting occurs from a different crystal structure. It is common to observe several different crystals that melt to either a mesophase or an isotropic liquid as the chain length increases. Of course, this is related to how the chain length can effect the packing of molecules in the solid phase. The only way to eliminate the effect of transition temperature is to compare the total enthalpies of melting i.e. crystal-crystal-mesophases-isotropic liquid. This was done in the early work with homologous series of cholesteryl esters [310] but is no longer done.

Many of the early DSC studies are done using cholesteryl esters showed rising melting curves with increasing chain lengths [310,311]. However, most enthalpy of melting curves show a lot of random variation in the shorter chain segment of

these curves. It is now obvious that there is even more randomness in plots of enthalpy values than in transition temperature curves for homologous series. It is also clear that a longer chain length will ultimately lead to larger enthalpy values for the melting transitions in such series rising sometimes even before the melting curve begins to rise [330].

A comparison of enthalpy with temperature plots for a number of homologous series shows the large variations that can occur [327] Similar comparisons for the two standards used in this report phenylbenzoates

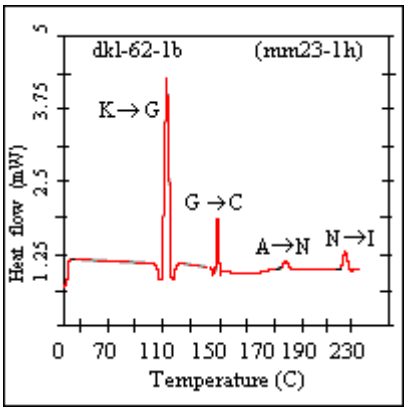


FIGURE 11

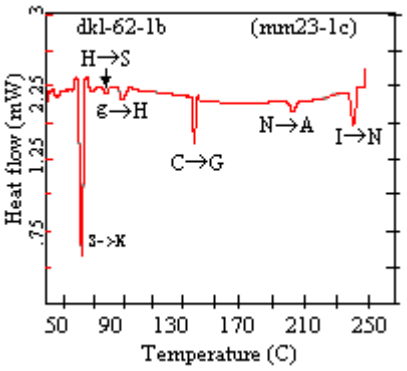


FIGURE 12

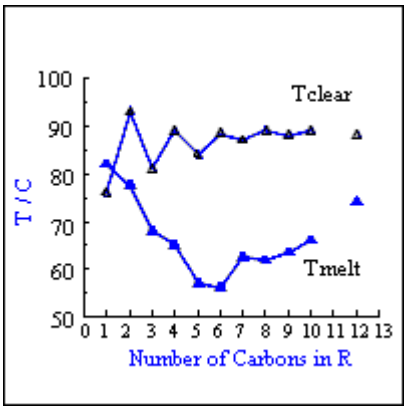


FIGURE 13

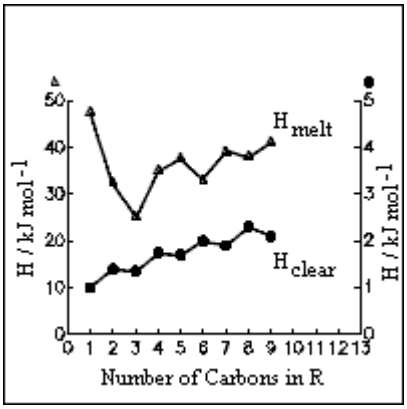


FIGURE 14

and cyanobiphenyls

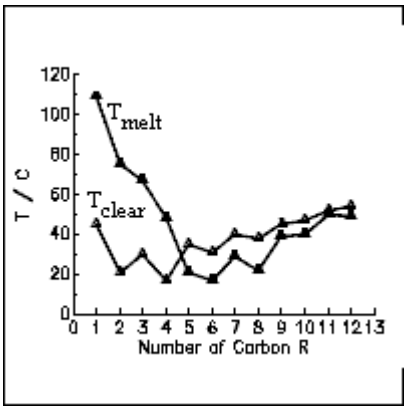


FIGURE 15

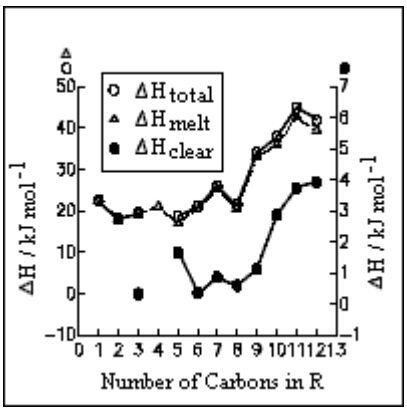


FIGURE 16

show similar melting temperature plots but different enthalpy of melting curves. In the PB series, the melting enthalpy curve falls to a minimum and then rises, levels off and rises again showing some resemblance to the melting temperature curve. However, the minimums in these two curves do not occur at anywhere close to the same homolog.

In the CB series, both the enthalpy of melting and clearing curves gradually rise with some alternation at the shorter chain lengths. This alternation is odd-even for the PB series but not for the CB series. Odd-even alternation occurs in both clearing curves. This alternation occurs in other series as well, but seemingly not as often as the alternation in clearing temperatures. A plot of the total enthalpy values pretty much parallels the melting enthalpy curve since the

enthalpies for the mesophase transitions are small. There is however, a greater separation at larger chain length.

Despite the large effect that chain length has on enthalpy values, attempts have been made in the literature to give a range of values for each type of mesophase transition without considering chain length. [327] Even in series showing only nematic phases, melting enthalpies increase with increasing chain lengths [332]. Still, using data for 391 mesogens, the following trends in enthalpy values were observed with the maximum values (kJ/mole) indicated:

insert equation

Generally, the trend observed is that expected i.e. melting values are larger than clearing and these are larger than mesophase transitions. One exception stands out - the smectic B-C transition perhaps because such transitions occur only in mid to long chain length mesogens. It would be interesting to see if this trend would hold with the considerably larger collection of enthalpy values now available in the Vill database.

Still, the range of values for a particular transition can vary over a considerable range. For example, of the 391 compounds studied, melting enthalpies varied from 1.7-28 k cal/mole, N-I from 0.02-2.30 and SC-t from 2.4-10.2. These ranges would likely be larger in our considerably larger collection of data today. Obviously, overlapping can occur so that using enthalpy values to assign types of phase transitions is rarely useful except in a general sense (i.e. melting is usually the largest value). Small enthalpy values can have a larger error and are difficult to compare [333].

Since enthalpy is directly related to the temperature D H = TD S, it is not surprising that the enthalpy values will increase as temperature increases and this often happens as chain length increases. However, as previously discussed, melting enthalpies often increase in a homologous series when melting temperatures do not. That leads to consideration of the effect of entropy changes. As the chain length increases, the molecule becomes more flexible and disordered on going from the presumed all trans configuration in the highly ordered crystalline state to the more disordered mesophase or liquid phase. Obviously, some mesogenic structures would be more flexible and disordered at shorter chain lengths contributing to increasing the range of reported enthalpy values.

Other chain modifications can also affect enthalpy values [334]. Strongly polar liquid crystals tend to have larger melting enthalpy values due to the strong-lattice forces between the molecules in the solid state. [307,192]. This is not surprising, since highly polar mesogens often have higher melting temperatures. A comparison of the melting enthalpy values for a variety of polar mesogens indicates the following order for these values: [335].

OMe>CN>CH_3>H>Cl>F>NO_2>Br

An early comparison of the melting enthalpy values for a variety of steroid esters suggested that enantiotropic mesophases tended to form when D S<40 cal/mole/° K whereas monotropic mesophases occur at larger values and no mesophases [336] at the highest observed values of ca [48]. Later work, however, has shown enantiotropic mesophases can occur in other structures having entropy values of 40 cal [327]. Thus far unanswered is whether our larger current collection of data would yield a new cut off entropy value. It seems reasonable since mesomorphic properties are ultimately lost in a homologous series when the terminal chain is made long enough. Like temperatures, it is a factor that is likely to be related to the entire molecular length.

Isotropic Phase

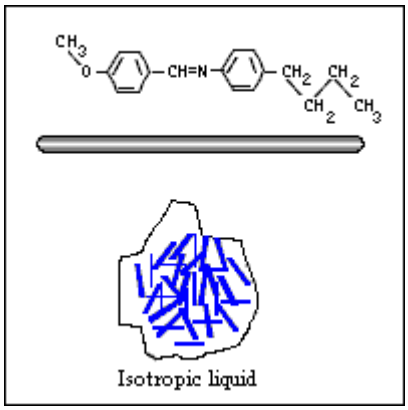


FIGURE 17

The shape of this molecule is anisotropic. X-ray diffraction intensity profile for this molecule above 81^0C is shown in figure 17

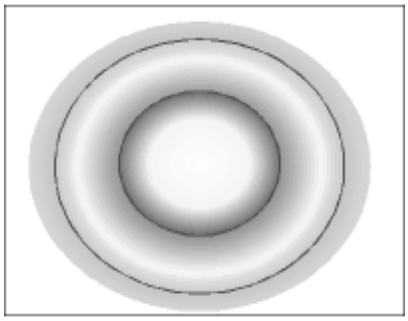


FIGURE 18

The full three dimensional profile of the sample reveals that the orientation and the position of the molecules are randomly distributed. Two rings correspond to the length and the diameter of the molecule. Under optical microscope, it appears completely dark. The physical properties, for an example viscosity, is independent of the direction which it is measured. The system possesses full rotational and translational symmetry. It is an isotropic liquid.

Nematics

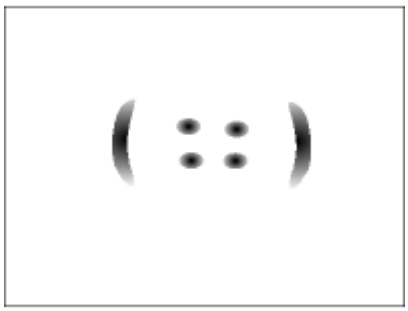


FIGURE 19

When the isotropic liquid cooled down below 81^0C, the x-ray pattern change into one shown in figure 19. This indicates that the molecules are on average parallel to an axis but their centers of mass still remain distributed randomly.

Optical microscopy

While the sample is cooling down, a sudden change at 81 ^{0}C can be observed under polarizing microscope. The sample turns to the texture shown in figure 20. This phase is called nematic derived from the Greek word "νημα" meaning thread. When the glass cover plates are treated with specific surfactants, the molecules can be aligned either perpendicular or parallel to the cover plates. Perpendicular alignment is known as homeotropic figure 21and parallel alignment is known as planar figure 22.

FIGURE 20

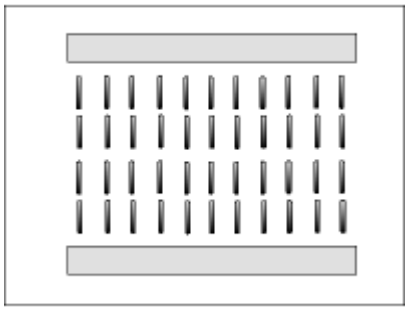


FIGURE 21

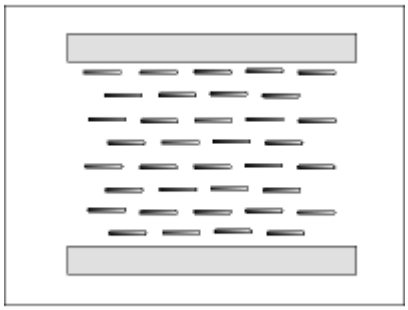


FIGURE 22

In nematic phase, molecules are aligned, on average, parallel to a particular direction which can be indicated by a unit vector **n** called director. Rotation of the system about an axis parallel to the director leave the nematic phase unchanged but not about an axis perpendicular to it. The three dimension rotational symmetry of the isotropic phase has reduced into one dimension in nematic phase. But the translational symmetry has not changed. The average orientation of the molecules which is the measure of the degree of order in nematic phase is given by

$$S = \frac{1}{3}\langle 3Cos^2\theta - 1\rangle$$

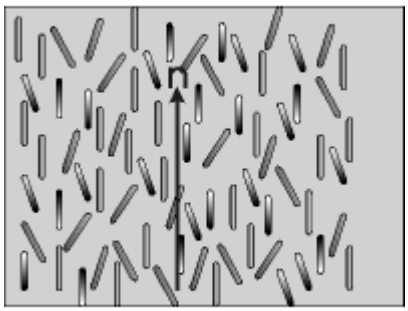


FIGURE 23

The nematic occurs directly below the isotropic phase and is characterized by

- elongated molecules

Molecular length >> width.

- optically uniaxiality

All the known thermotropic nematics are uniaxial.

- orientational order but no long range positional order
- molecules may or may not have permanent dipole moments
- $\hat{n}$ and $-\hat{n}$

are equivalent

Smectic A

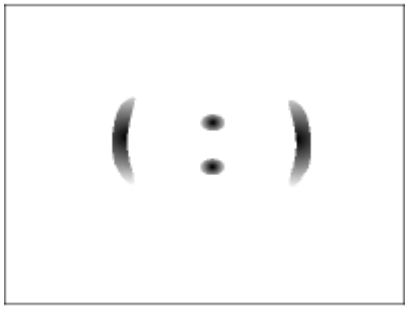


FIGURE 24

When the material in nematic phase cooled down below 37 ^{0}C, the x-ray pattern change into one shown in figure 24. Out side rings remain as it was in nematic but inner rings have turned into sharp points. This indicates that the molecules are still aligned parallel but their centers of mass are no longer distributed randomly in three dimension.

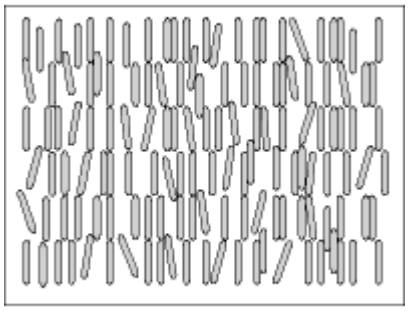


FIGURE 25

In smectic A phase, molecules are situated parallel to each other in well defined layers. The layer spacing is approximately equal to the length of the molecules. Inside the layers, molecules move like in liquid and there is no correlation among molecules in adjacent layers.

When nematic is cooled down, The texture abruptly changes at 37 ^{0}C. The resulted texture known as "focal conic" is shown in figure 26.

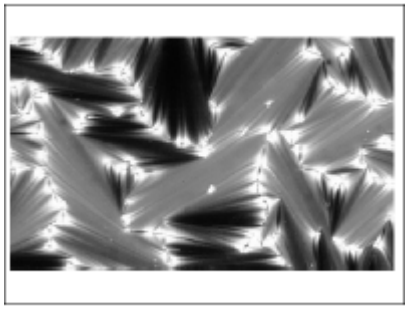


FIGURE 26

Smectic layers are flexible and slide over each other. Uniformity of the layers can be easily distorted but tend to preserve interlayer spacing. Smectic A phase is optically uniaxial. Homeotropically aligned smectic A sample can not be distinguished from homeotropically aligned nematic sample by optical microscopy.

Smectic A phase is rotationally symmetric with respect to an axis perpendicular to smectic layers. Due to the fact that molecules are situated in layers, there is no full translational symmetry in the direction of layer normal. The translational symmetry in nematic phase has now reduced in smectic A phase from three dimension to two dimension. The translational symmetry preserved only in two dimension inside the layers. The smectic A phase however does not have the true long range periodic order since thermal fluctuation destroy the long range periodicity of the layers. The order of the smectic A phase can be described by sinusoidal modulation of the density wave perpendicular to the layers given as

Twist Gain Boundary (TGB) phase (Smectic A*)

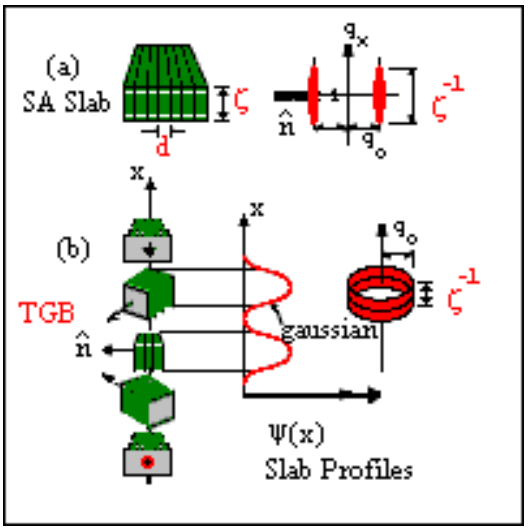


FIGURE 27

Smectic A* is composed of optically active molecules. Unlike smectic C* whose helical axis normal to the layers, smectic A* has its helical axis parallel to them.

Hence the structure may be looked upon as a series of smectic blocks or grains separated by twist gain boundaries. The director which in this the layer normal is rotated by a constant angle on going from one grain to the next. From observation of the reflection of circularly polarized light incident along the helical axis it is found that the pitch is of the order of 1 micro meter. X-ray measurement reveals that the grain size is about 180 ^{0}A

Smectic C

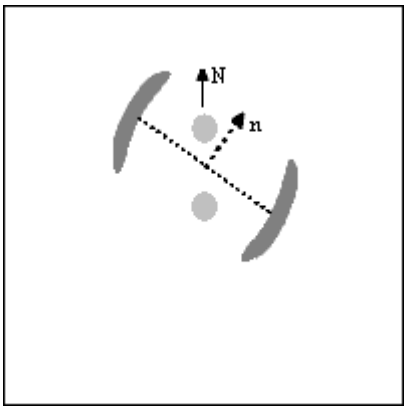


FIGURE 28

When the material in Smectic a phase is further cooled down below 37 ^{0}C, the x-ray pattern change into one shown in figure 28. Out side rings remain as it was in smectic A but tilted with respect to inner points. This indicates that molecules are still in layers but they are tilted with respect to the layer normal.

FIGURE 29

The optic axis of the system is tilted with respect to the layer normal so that smectic C phase is optically biaxial. Under conoscopic setup, optical microscopy shows split cross at an extinction which is typical of biaxiality. This can be observed in a thin sample cells with parallel alignment.

Similar to smectic A phase, focal conic domains can still be seen in smectic C phase as well. There are additional textures can be seen in smectic C phase as a result of the tilted structure.

FIGURE 30

Smectic A phase can be distinguished from smectic C phase by microscopic observation of homeotropically aligned samples. Unlike in smectic A phase, long axis of the molecules are not perpendicular to the sample cell anymore.

While the one dimensional symmetry of the system remained unchanged, the rotational symmetry has been reduced in smectic C phase. It now has two fold axis within the layers. Molecules are tilted in preferred direction inside the layers and tilt direction of the molecules in various layers are correlated. Therefor their projection in the plane of the layers are aligned in a common direction. This is usually denoted by a unit vector c called c - director. The system remains invariant for the transformation in director n to -n but not for c director. Measure of the order of smectic C can be given by

$$c = \theta \exp(i\phi)$$

where q is the tilt angle and f is the azimuthal angle.

Hexatics

Characteristic of smectic A and C phases is that the molecules are stacked in layers. Inside the layers, molecules are distributed randomly. When some systems cooled down further, it has been observed in X- ray studies that the molecules are distributed in a hexagonal lattice within the layers. A variety of these structures have been observed. These phases are referred to as the hexatic phases with short range positional order and long range bond-orientational order (bond in this case is the line joining the center of molecules of nearest neighbors). The relevant order parameter for the six fold bond-orientational order is

$$\psi = \exp[i6\theta(r)]$$

where $\theta(r)$ is the angle between the local lattice vectors or bonds and some reference axis.

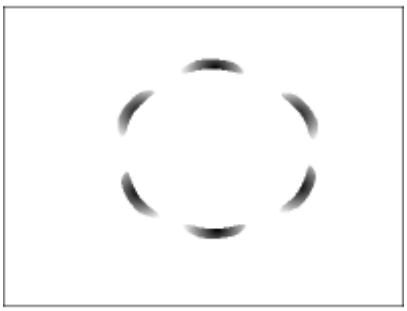


FIGURE 31

Detail x-ray studies reveal that there are many type of hexatic phases.

Smectic B

Two distinct smectic B phases have been identified. Both of these phases, molecules are aligned perpendicular to smectic layers. Three dimensional crystal, **crystalline B** phase, has short range positional correlation among layers with molecules in hexatic two dimensional lattice. Hexatic B forms layers with short range positional correlation and week correlation between layers.

Smectic D

This phase occur between S_C and S_A or between S_C and the isotropic phase. The mechanism of structural formation and the detail molecular arrangement is not known but assumed to be micelle type. At present only 4 compounds are known to exhibit this phase.

Smectic E

Three dimensional crystal, orthorhombic with interlayer herringbone arrangement of the molecules.

Smectic F

This is the tilted version of the hexatic B phase. There are two types of smectic F, chiral and achiral. Achiral Smectic F has the C- centered monoclinic symmetry with in-plane short-range positional correlation and weak or no interlayer positional correlation. Chiral Smectic F is formed with a twist axis normal to the layers.

Smectic G

It has a C- centered monoclinic symmetry.

Smectic H

There are two types, chiral and achiral. Three dimensional crystal, monoclinic, with herringbone arrangement of the molecules. Chiral Smectic H is form with a twist axis normal to the layers.

Smectic I

There are two types, chiral and achiral. Achiral Smectic F has the C- centered monoclinic symmetry and tilted hexatic with slightly greater in-plane correlation than smectic F. Chiral Smectic F is form with a twist axis normal to the layers.

Smectic J

There are two types, chiral and achiral. Three dimensional crystal, monoclinic, with herringbone arrangement of the molecules. Chiral Smectic F is form with a twist axis normal to the layers.

Smectic K

There are two types, chiral and achiral. Three dimensional crystal, monoclinic, with herringbone arrangement of the molecules. Chiral Smectic F is form with a twist axis normal to the layers.

Discotics

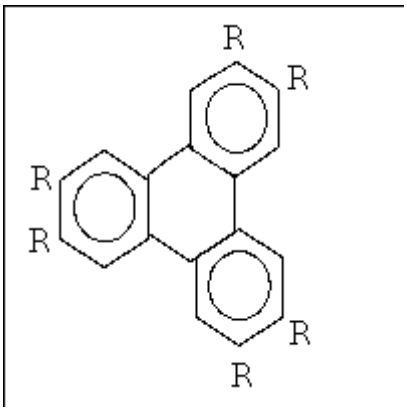


FIGURE 32

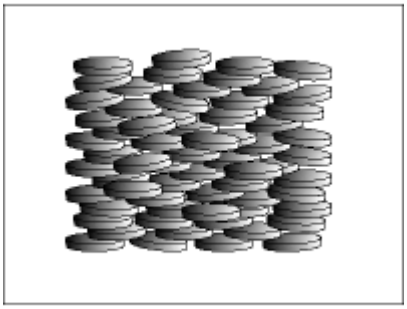


FIGURE 33

Nematic phase has been observed with molecules rather flat, disc like as in figure 17. In addition, a number of new type of phases are formed with disc like molecules that they can not be classified as nematic or smectic. This was first discovered by Chandrasekhar et al.. The disc like molecules are packed in columns such that they are ordered or randomly distributed inside the columns. The columns themselves can be arranged in hexagonal or orthogonal lattice with six fold cylindrical symmetry. They exhibit optical anisotropy and nematic like textures. They can be aligned in external electric or magnetic fields.

Commensurate Phase

Commensurate means periodicity of any structure in space. Incommensurate structures are repeated in a few intervals without specific long range periodicity. The molecules of the type shown in figure 32 form structures which neither periodic nor random. These molecules which possess large longitudinal dipole moments form variety of polymorphic Semitic phases known as frustrated smectic or incommensurate smectic phases. The phases exhibited by such systems have several smectic density waves coexisting simultaneously. The

polymorphism of these molecules was first discovered by Signard and latter theoretically described by Prost, Barias and Lubensky.

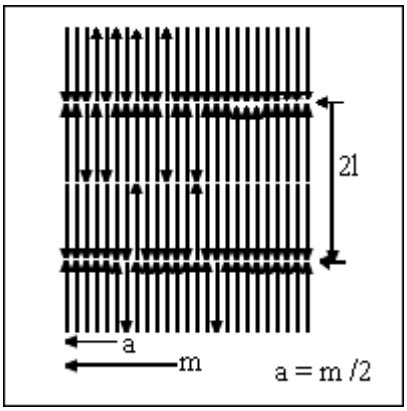
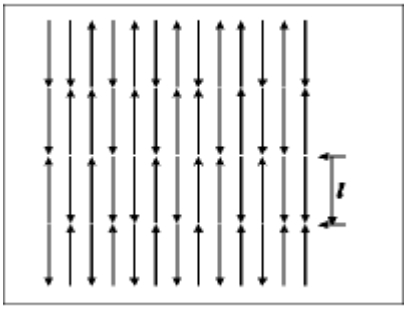


FIGURE 34

The length and large off centered dipole moment of the molecules seem to have an effect on the liquid crystalline phases they form. There are two important length scales, the molecular length l and the pair length 2l' as shown in figure



32.

FIGURE 35

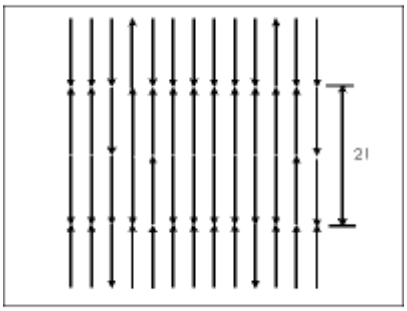


FIGURE 36

Several new smectic phases have been reported with these type of systems. In particular, Sm A_1, bilayer Sm A_2, partially bilayer Sm A_d , fluid anti phase Sm $\tilde{A}$ and antiphase Sm $\tilde{C}$.

Chiral Liquid Crystals

When a molecule is not equal to its mirror image, it is called a chiral molecule. Compounds of chiral molecules are strongly optically active. Chiral compound form liquid crystalline phases with very interesting optical and electro-optic properties. Liquid crystalline phases can also be modified by adding chiral molecules to those of non chiral.

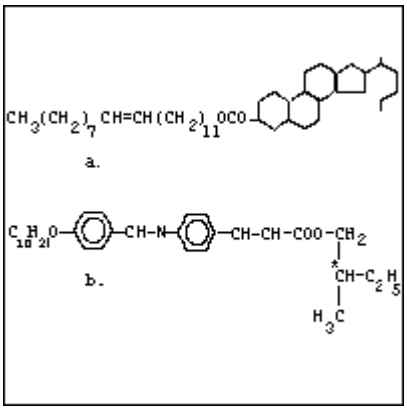


FIGURE 37

LIST chiral phases.

Cholesteric liquid crystals

Cholesteryl benzoate which is a chiral compound lead Reintzer to discover the liquid crystalline phases in 1898. When chiral molecules are added, nematic phase is changed to spatially modified cholesteric phase knows also as twisted nematic. While the order of the cholesteric phase remains as same as nematic, the director makes a twist about an axis with a constant angle.

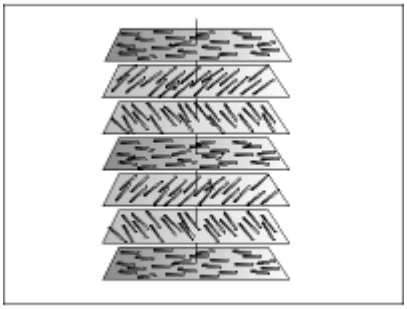


FIGURE 38

Twisted structure of the cholesteric phase give rise to optical rotation and selective reflection. Selective reflection takes place when white is incident on a sample with planar alignments where optic axis of the sample is perpendicular to the glass plates. At normal incident, reflected light is circularly polarized. One component is completely reflected while the other transmitted unchanged.

Ferroelectric liquid crystals

Condensed materials which exhibit permanent electric moment in the absence of an external electric field are called ferroelectric in analogy with the well known ferromagnetic effect. Barium Titanate, $BaTiO_3$, is an example of a ferroelectric material. The orientation of the permanent polarization (spontaneous polarization) can be reversed by an external electric field. Solid crystals which are ferroelectric seem to have monoclinic symmetry.

The ordinary smectic C liquid crystals can transform into a modified phase called C* when optically active materials are added. In the C* phase, molecules are twisted along an axis perpendicular to the smectic layers. Optical properties of SC* are similar to cholesterics when light is propagating along the axis of the twist. When the incident light makes an angle with twist axis additional features can be seen.

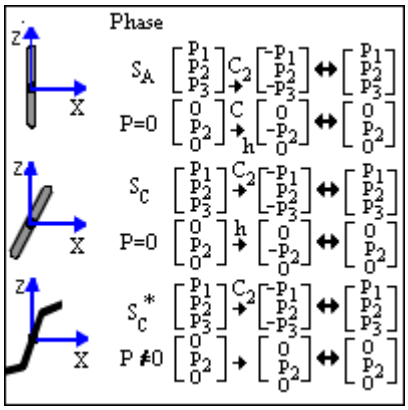


FIGURE 39

In 1975, using symmetry arguments, R. B. Meier[16] showed that the smectic C phase is ferroelectric. As mentioned earlier, the liquid crystal molecules have permanent dipole moments. These dipole moments in general make an angle with the long molecular axis, thus each molecule has a component of dipole moment perpendicular and parallel to the long axis. Even though individual molecules are polar, due to up-down symmetry and rotational symmetry, system all together is non polar. As shown in the figure 1.2, an axis system is defined such that in the smectic phase, the Z axis is parallel to the layer normal and X and Y axes are coplanar with the layers. In smectic A phase molecules are free to rotate around the Z axis and have a two fold rotational symmetry about X and Y axes. Molecules are also symmetric about the mirror planes which are Z-X or Z-Y. These symmetry operations will prevent existence of permanent polarization. In smectic C, each layers is a two dimensional liquid and has a monoclinic symmetry. Tilted molecules in smectic C do not have arbitrary rotational symmetry. But the mirror symmetry will still cancel out the permanent polarization. If the molecules are chiral, both mirror symmetry and center of inversion no longer exists. In this case the only symmetry axis that remains is the axis perpendicular to the long molecular axis and parallel to the smectic layers . However as in the cholesteric phase, molecules in Sc* phase also form a helical structure making the spontaneous polarization vanish in the bulk. Due to the tilt of the chiral molecules, the component of the dipole moment

along this remaining symmetry axis will not average out to zero allowing a net permanent polarization.

Liquid Crystal Mixtures

Liquid crystal mixtures are important in many ways. The complete miscibility study was the criterion originally used for the identification of different liquid crystalline phases. The liquid crystal mixtures are used

- to widen the temperature range of phases.
- to investigate interaction between order parameters in different phases
- to investigate pretransitional behavior
- to identify unknown substances by mixing with substances with well known phase behavior

Mixtures are also used to create new phases such as chiral nematics or smectic by mixing chiral molecules into ordinary liquid crystals.
Nematic mixtures
There are many nematic eutectic mixture with thermodynamic stability. Nematic mixture are of great interest in many liquid crystal applications. The best liquid crystal material for displays are multi-component mixtures which have a wide temperature range.

Reentrant nematic phase

Unusual phase transition sequence was observed by Cladis in mixtures of p-cyanobenzilidene-p'-butylaniline and p-hexyloxybenzinidene amino benzonitrile. This is known as the reentrant nematic where nematic phase is followed by smectic A -reentrant nematic phases when the temperature is decreased. There have been several other compound identified with the same behavior. The parabolic shape of the phase diagram is described by taking translational and positional order into account. Macroscopic explanation is based on the frustration phenomena due to the competition between steric and dipole-dipole interactions.

FIGURE 40

Mixtures of Chiral molecules and achiral molecules

When a chiral molecules (dopant) are mixed with achiral molecules in nematic phase, nematic phase with twisted structure known as chiral nematic is formed. When a chiral molecules are mixed with achiral molecules in smectic C phase, ferroelectric phase is formed. Dopant itself may or may not have a liquid crystalline phase. Resultant compounds have a helicoidal structure characterized by helical pitch and its sign. The wave vector which is the inverse of pitch strongly depend on the concentration of the dopant in the mixture. In smectic case, the dopant induces a spontaneous polarization P_S. The magnitude of the polarization is proportional to the concentration of the dopant. Mixing two chiral smectic compounds, magnitude of the polarization, magnitude and the sign of the pitch can be controlled. Both of these mixtures, chiral nematic and ferroelectric, have features that are very important in technological applications.

Lyotropic Liquid Crystals

Lyotropic liquid crystals are multi component systems formed in mixtures of amphiphilic molecules and a polar solvent. Amphiphilic molecules are consisted of a hydrophilic polar head attached to a hydrophobic hydrocarbon tail containing one or two alkyl chains.

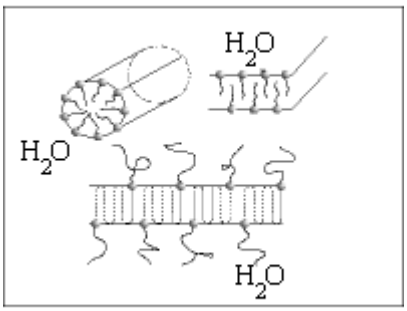


FIGURE 41

When amphiphilic molecules called surfactant are added into a polar solvent, true molecular mixtures exist at low surfactant concentration. After exceeding a critical concentration, they tend to aggregate micelles so that the polar groups occupy the interface towards polar solvent. The size of the aggregates normally comparable to a few molecular lengths and spherical in shape.

Nematic Phase

When the surfactant concentration is further increased, micelles can turn to disc like, cylindrical and ellipsoidal shapes. These micellar structures give rise to several nematic phases. N_L denotes a nematic phase in which the micelles are disc like with lamellar structure. Optically N_L is uniaxial. Over a small concentration range, the system can turn to N_C phase with cylindrical micelles. If the temperature is lowered at this concentration, N_L phase is reappeared. These two phases are separated by an intermediate biaxial phase, in fact the only biaxial nematic phase experimentally ever observed, denoted by N_{bx}.

Micellar Cholesteric phase

A twist can be induced into uniaxial amphiphilic nematic by adding chiral molecules or by chiral amphiphilic surfactant. The induced twist is proportional to the concentration given by

$$\frac{1}{p} = \alpha C$$

where C is the concentration of the chiral additive and is the power of twist.

Smectic Phases

If surfactant concentration is increased further, Smectic phases known as middle soap or hexagonal are formed by cylindrical micelles. The polar groups sit now on the surface of a cylinder and the cylinders are arranged parallel in a hexagonal packing. The microscopic textures of the hexagonal phase show some similarities with the texture of lamellar smectic phases. Textures resembling a fan texture and a focal conic texture can occur but there are characteristic differences, for instance no disclination lines of focal conic shapes are present. In addition a typical striated texture without well defined geometrical features may form A pseudo isotropic texture has not been observed. From isotropic solutions, it precipitates in batonnets or in circular droplets.

At much higher concentrations lamellar structures are formed. In case of water solvent, the lamellas or double layers are arranged parallel and separated by a thin film of water. Amphiphilic layers are formed with the hydrocarbon tails filling the inner part of the layer and the polar groups forming the interface against water.

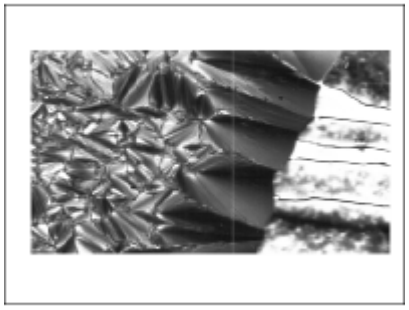


FIGURE 41 lamellar

The thickness of the lamellae is in general smaller than twice the length of the stretched amphiphilic molecules. When temperature and water content is increased, the thickness of the lamellae decrease as the hydrocarbon chains tend to form coils.