

CHAPTER 3

Liquid Crystalline State of Matter

3.1 Introduction

Sometimes referred to as the fourth state of matter, the *liquid crystalline state* possesses the properties of both a liquid and a solid. The liquid crystalline state is usually associated with small molecules, but many polymeric systems exhibit similar types of order to those found in low molecular weight liquid crystals. It is appropriate to consider the factors that influence the formation of liquid crystalline phases in small molecules before considering polymer systems.

3.1.1 The Liquid Crystalline State

Whereas a perfect crystal exhibits a high degree of order, liquids possess total disorder. Between these extremes of crystalline order and liquid disorder, lie phases characterized by varying degrees of organization. The least ordered state is the *nematic* phase, the molecules in this phase being aligned in only one direction. The *smectic* phases correspond to molecules ordered in two directions and yet disordered in the third direction. The *smectic* phases correspond to various different types of partially ordered arrangements and resemble closely the crystalline phase of matter, discussed in Chapter 2. Many of the rules concerning molecular design and order observed for small molecules, and presented in this chapter, are also relevant to polymeric liquid crystalline materials.

3.1.2 Historical Perspective

The Austrian botanist Reinitzer,¹ when heating cholesteryl benzoate, observed a melting point at 145.5 °C, leading to a cloudy liquid which cleared at a temperature of 179.5 °C. He had discovered *cholesteric* liquid crystals. In 1922, Friedel² described a variety of different liquid crystal phases and proposed a classification scheme consisting of the three broad classes: *nematic*, *cholesteric* and *smectic* materials.

3.1.3 Mesophase Order

Mesophases or *mesomorphic* phases are intermediate between solid and liquids and the molecules that exhibit this type of behaviour are termed *mesogens*. Most liquid crystals are organic molecules, and exhibit liquid crystalline behaviour over a defined temperature or concentration range or have order induced by the application of an external magnetic or electric ordering force. Liquid crystals that change their order with temperature are called *thermotropic*, whereas those that change with concentration of solvent are called *lyotropic*. A general feature of all liquid crystal materials is that the molecules have a rod-like characteristic, but, with a greater width than thickness, a better description would be lath-like in shape. However, the existence of a liquid crystalline phase is usually associated with a degree of rotational freedom around the molecular long axis, allowing the molecule to sweep out a cylinder by rotation. Most liquid crystals will possess some limited degree of flexibility.

3.1.4 Nematic Liquid Crystals (N)

The characteristic morphology of the liquid crystalline phase is usually observed using crossed polarized microscopy. The designation *nematic* comes from the Greek word νημα, which is the word for 'thread' which typifies the structures exhibited by this phase. These 'threads' correspond to lines of singularity in the *director* alignment called *disclinations* that are the disruption of the continuity of the *director*. The polarized light imposes on the system a reference alignment direction that probes the preferred direction of alignment of the molecules (Figure 3.1), which is indicated by the *director*. In *nematics*, this direction is referred to as the *anisotropic* axis and there are no long-range correlations between the centres of mass of the molecules. In the *nematic* phase, free translation is allowed in the direction of alignment whilst being constrained to remain approximately parallel to one another. Free rotation can occur around the anisotropic axis, with the result that the *nematic* phase is uniaxial and will have no polarity, although the constituent molecules may have polarity.

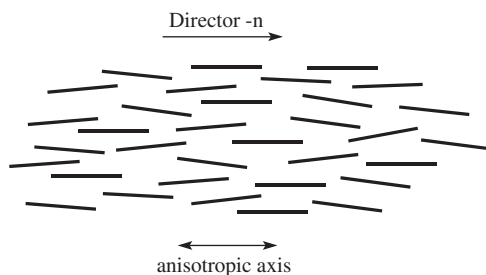


Figure 3.1 Schematic representation of a *nematic* liquid crystal phase. The lines represent the molecules and the unit vector \mathbf{n} , called the *director*, describes the average direction of the molecular alignment along the uniaxial anisotropic axis.

3.1.5 Smectic Liquid Crystals

The word *smectic* comes from the Greek word $\sigma\mu\eta\gamma\mu\alpha$, meaning ‘soap’ and reflects the mechanical properties displayed by many of these materials. All *smectics* are layered structures having well-defined interlayer distances. *Smectic* materials are therefore more ordered than *nematic* ones and occur at a temperature below that for the *nematic* phase. A number of smectic phases have been identified.³

Smectic A: S_A . Smectic A has a structure in which the molecules are arranged in layers, as shown in Figure 3.2a, but the molecules are disordered within the layers. In *thermotropic* liquid crystals, the *smectic* layer thickness may vary from a value that is closer to the length of the molecule to a value that is almost twice this value⁴ and is typically in the range 20–80 Å. The lyotropic smectic A phase can have layer thicknesses up to several thousand angstroms. The director \mathbf{n} represents the average molecular orientation of the molecules.

Smectic B: S_B . The *smectic* B phase is similar to the *smectic* A phase in that the molecules are aligned perpendicular to the layers but the molecules are in this case hexagonally close packed within the layers and are usually one molecule thick. The necessary disorder for these to be a liquid crystalline phase arises from rotation of the molecules about their long axis. It would be untrue to say that they are ‘free’ to rotate, but the molecules do not exhibit a well-defined orientation one to another (Figure 3.2c)

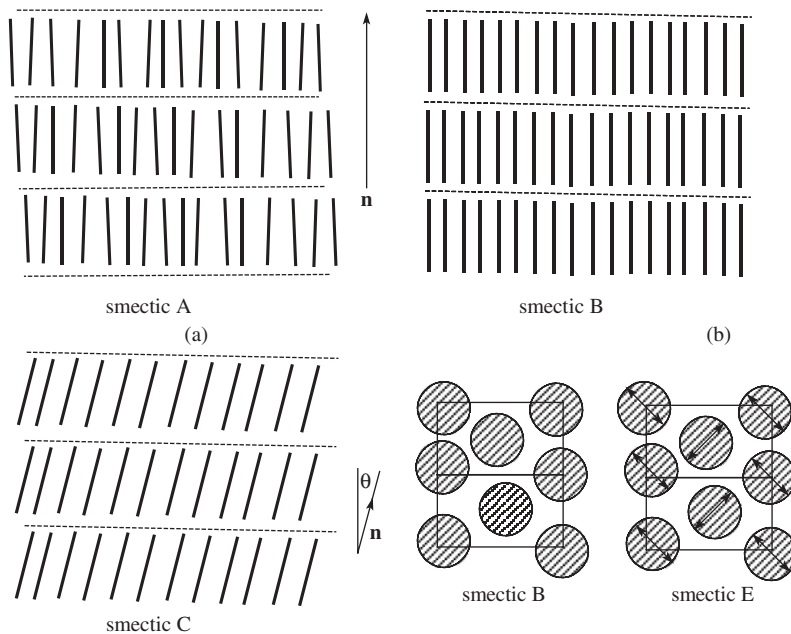


Figure 3.2 Schematic of the molecular orientation in smectic phases.

Smectic C: S_C . The alignment in the *smectic* C phase is similar to that in the *smectic* A phase except that the director is tilted at an angle θ relative to the layer normal (Figure 3.2b). The angle θ is usually temperature dependent and is called the *smectic* C tilt angle or *smectic* cone angle. The director \mathbf{n} continues to be defined as the average direction of the molecular alignment. *Chiral smectic* C phases can occur when the constituent molecules are enantiomorphic. *Chiral smectic* C materials exhibit a helical structure in an analogous way to the ‘twisting’ that takes place across the *smectic* layers, the helical axis being in the direction of the layer.

Smectic E: S_E . Although the *smectic* E phase may occur on its own or in conjunction with a higher temperature *nematic* phase, it is most commonly encountered in the sequence of phases $N \rightarrow S_A \rightarrow S_B \rightarrow S_E$, where the arrows indicate decreasing temperature.

Other smectic phases. Other smectic phases have been observed, where each phase relates to a particular type of crystal structure as defined in Chapter 2. For instance, smectic D is associated with a disordered cubic structure,⁵ smectic H appears to be a tilted smectic B phase⁶ and the smectic G phase has close similarities with the smectic E phase but is tilted.⁷ A list of smectic phases is presented in Table 3.1.

3.1.6 Cholesteric Liquid Crystal (C)

Cholesteric liquid crystals are similar to nematic phases except that the molecular orientation between one layer and the next shows a progressive helical order. This helical structure arises from the chiral properties of the constituent molecules. Chiral molecules differ from their mirror image and have a left- or right-hand sense and are called enantiomorphic. The *director* is not fixed in space and rotates throughout the sample as shown in Figure 3.3.

3.2 Influence of Molecular Structure on the Formation of Liquid Crystalline Phases

A number of molecular factors influence whether or not liquid crystalline behaviour is observed within a specific molecular structure. These factors are also relevant when considering the behaviour of polymeric materials.

3.2.1 Influence of Chain Rigidity

The *n*-alkanoic acids (long-chain fatty acids) exhibit liquid crystalline characteristics. The alkane chain can be represented in an all-*trans* structure that gives the molecules the required high aspect ratio; however, being very flexible it will allow the dimer to readily form a crystalline structure. If, however, double bonds are now introduced into the structure in the form of alka-2,4-dienoic acids,^{8,9} the structure is now sufficiently rigid, due to restricted rotation about

Table 3.1 Structural classification of smectic phases.^{20,58}

<i>Smectic</i>	<i>Comment</i>
A (S_A)	Liquid-like layers with upright alignment of molecules
B (S_B)	Two distinct types of S_B have been identified: <ul style="list-style-type: none"> • Three-dimensional (3D) crystal, hexagonal lattice, upright alignment • Stack of interacting ‘hexatic’ layers with in-plane short-range positional correlation and long-range 3D six-fold ‘bond-orientational’ order
C (S_C)	Tilted form of S_A
C* (S_{C^*})	Chiral S_C with twist axis normal to the layers
D (S_D)	Cubic
E (S_E)	3D, orthorhombic upright alignment
F (S_F)	Monoclinic ($a > b$) with in-plane short-range positional correlation and weak or no interlayer positional correlation (tilted hexatic type of structure)
G (S_G)	3D, monoclinic ($a > b$)
G' ($S_{G'}$)	3D, monoclinic ($a > b$)
H (S_H)	3D, monoclinic ($b > a$)
H* (S_{H^*})	Chiral S_H , with twist axis normal to the layers
H' ($S_{H'}$)	3D crystal, monoclinic ($b > a$)
I (S_I)	Monoclinic ($b > a$) possibly hexatic with slightly greater in-plane positional correlation than S_F
I* (S_{I^*})	Chiral S_I

Many of the smectic phases are very similar and precise differentiation can be difficult between closely related phases.

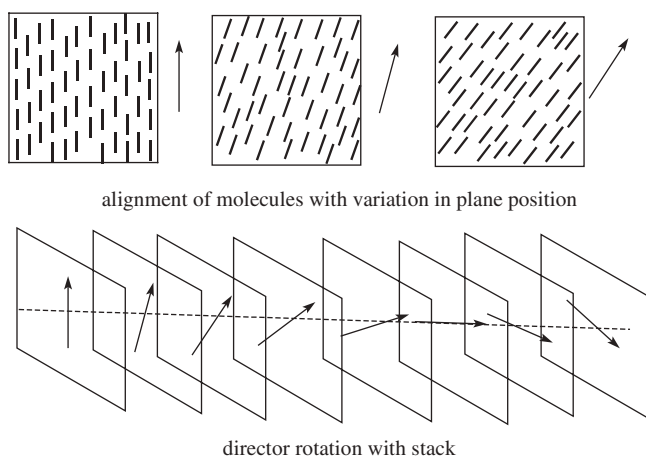
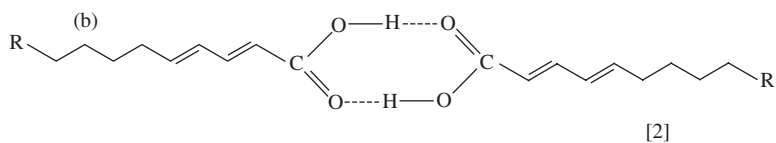
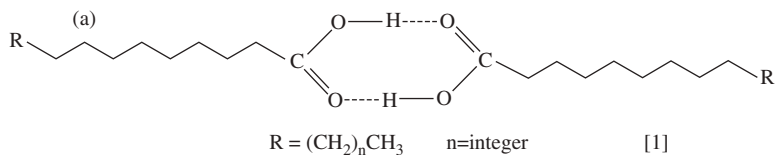


Figure 3.3 Schematic of the change of molecular alignment with stack sequence of a *cholesteric* phase. Each layer has *nematic* order.

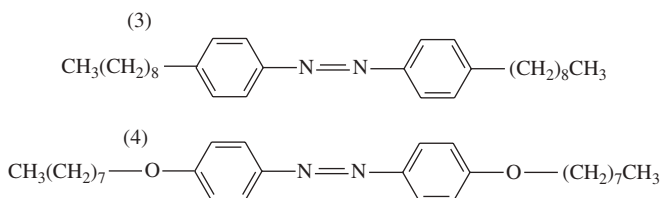
the double bonds of the sp^2 hybridized carbon atoms, for the compounds to exhibit *nematic* phase. Although the rigid sections would pack as for a crystalline structure, entropy will disorder the flexible saturated chains and inhibit crystallization.



Looking for molecular structures that lead to liquid crystal behaviour, it is found that most molecules have a flexible chain in addition to a rigid element. Incorporation of a flexible chain generates the entropic disorder that inhibits the molecules forming crystalline structures. Theoreticians are able to consider the statistical mechanics of liquid crystals in terms of hard particles (rods, spheres, discs, *etc.*), but to understand the detailed behaviour we need to look at the molecular interactions in detail.

3.2.2 Influence of Size of Rigid Block

Whether a particular molecule will exhibit liquid crystalline characteristics depends upon the balance in inter- and intramolecular interactions. For instance, we can compare the following two diazomolecules:

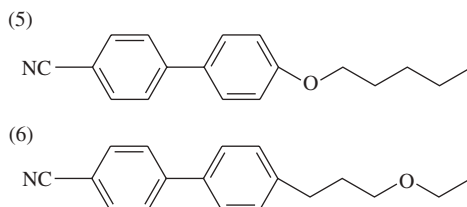


Both molecules **(3)** and **(4)** have similar rod-like structures with the same number of atoms in the terminal chains. Unless the small differences in the bond angles and bond lengths between the C–C and C–O bonds have significance, it is difficult to explain why **(3)** exhibits two *smectic* phases with crystalline (C) to *smectic* B (S_B) transition temperatures¹⁰ at 37 °C, S_B to S_C at 40.5 °C and S_A to isotropic (I) (liquid) at 53 °C, whereas **(4)** exhibits only a *nematic* phase with very different temperatures: C to N at 102 °C and N to I at 109 °C. An important difference between these apparently similar molecules is that the C–O bond will be conjugated to the aromatic ring and hence the length of the rigid element is

greater in (4). In addition, the intermolecular repulsions for the systems would differ, since the $-\text{CH}_2-$ and $-\text{O}-$ functions behave differently electronically.

3.2.3 Influence of Sequence Structure in Chain

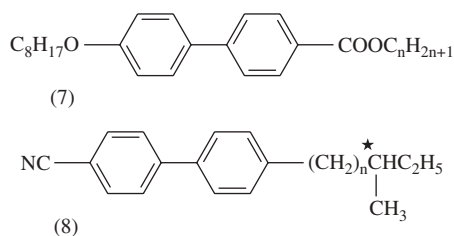
The cyano biphenyl molecules illustrate the effect of sequence structure on the ability to form various phases. The cyano biphenyl molecules form a very important group of materials being widely used in many liquid crystal display applications. Two examples are as follows:



These molecules have the same chain lengths but differ only in the location of the oxygen. Compound (5) melts at $53\text{ }^\circ\text{C}$ and gives a nematic phase and having a clearing point at $67.5\text{ }^\circ\text{C}$, whereas compound (6) melts at $36\text{ }^\circ\text{C}$ and forms no *nematic* phase even on cooling to $0\text{ }^\circ\text{C}$, when re-crystallization occurs.¹¹ Once more the principal difference between these molecules is that (5) has the oxygen partially conjugated with the phenyl ring, whereas (6) has an aliphatic ether link and the oxygen increases the flexibility of the aliphatic chain and introduces greater disorder in the melt.

3.2.4 Variations Within a Homologous Series of Molecules

Cooling esters with the following formulae



gives rise to a variety of different liquid crystalline phases depending on the value of n in the terminal chain.¹² The asterisk indicates a *chiral* centre in the chain. The sequence of phases observed for the alkylbiphenyl esters are listed in Table 3.2.

There are a number of factors working within this series of molecules. Firstly, a S_C phase appears at $n=4$, the S_B and S_E being also only observed for $n=3$. The alkyl cyano biphenyl molecules, structure (8), all have the same absolute

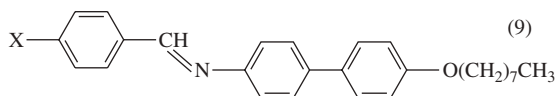
Table 3.2 The phases observed for a series of alkylbiphenyl esters, structure (7).

<i>Value of n in ester chain</i>	<i>Phase types observed on cooling</i>
2	I → S _A → S _B → S _E → C
3	I → S _A → S _B → C
4	I → S _A → S _C → C
5	I → S _A → C

configuration at the asymmetric carbon atom, indicated with an asterisk. The molecules with values of n from 1 to 3 all exhibit *cholesteric* phases. However, if they are mixed together 1 with 2 or 2 with 3 *nematic* phases are observed. On moving the branching point from an even to an odd to an even point in the chain the sense of the *cholesteric* helix changes from right handed to left handed and back to right handed again.¹³

3.2.5 Changes in Substituents

Changes in substituents will influence the electronic polarizability of a molecule. Consider the following structure:



Methyl and chlorine groups have very similar sizes, so that molecules with $X = \text{Cl}$ and CH_3 have the same rod shape.¹⁴ However, the transitions observed for these molecules are very different: when $X = \text{Cl}$, $\text{C} \rightarrow \text{N}$ occurs at 193°C and $\text{N} \rightarrow \text{I}$ occurs at 261.5°C ; when $X = \text{CH}_3$, $\text{C} \rightarrow \text{S}_A$ occurs at 178°C , $\text{S}_A \rightarrow \text{N}$ at 178°C and $\text{N} \rightarrow \text{I}$ at 222°C . Such differences in behaviour cannot be considered to be subtle. To understand why these differences occur, the *mesogen* must be considered to be a dynamic entity consisting of a fairly rigid section, the core of the structure, and a flexible part. The entire molecule may be freely rotating about some axis that may not be along the most obvious line, and precise consideration of the stereochemistry of the molecule is essential to determine the preferred axis. Superimposed on the effects of geometry are the intermolecular interactions that define the potential in which the molecules rotate and move. The Cl group will add an additional dipolar contribution that will be reflected in the higher transition to the isotropic phase.

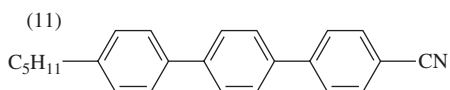
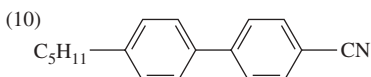
3.3 Common Features of Many Liquid Crystalline Forming Molecules

Mesogenic behaviour is associated with molecules having a rigid core section, that will often contain an aromatic element, but this is not essential. Attached

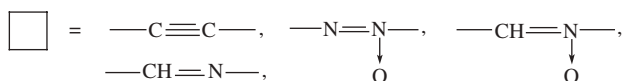
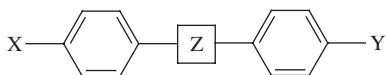
to the core will be a polarizable group, e.g. Cl, CN, NO₂, NMe₂, and also a long flexible chain. The latter allows the molecule to retain the entropic element that inhibits the formation of the crystalline phase. The flexible chain will usually be an alkyl or alkoxy group.

3.3.1 Nematic Liquid Crystals

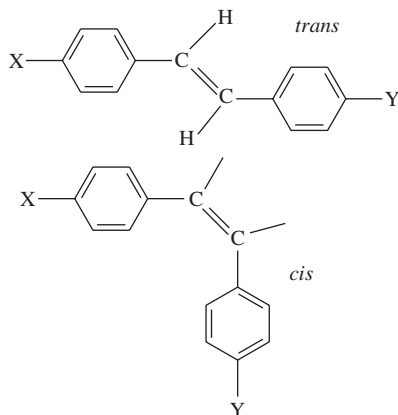
The rigidity of the central core structure is often achieved using aromatic rings, as in the case of 4-cyano-4'-*n*-pentylbiphenyl¹⁵ (**10**) or 4-cyano-4''-*n*-pentyl-*p*-terphenyl¹⁶ (**11**):



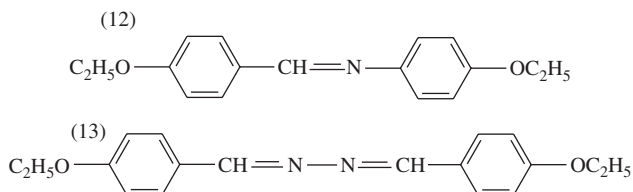
The biphenyl shows transitions C–N at 22.5 °C and N–I at 35 °C, whereas the terphenyl shows transitions C–N at 130 °C and N–I at 239 °C. In these molecules, planarity of the two aromatic rings is inhibited by strong interactions between the hydrogen atoms in the α -position to the C–C bond. Mesogenic behaviour is observed if the aromatic rings are joined by one of the following entities:¹⁷



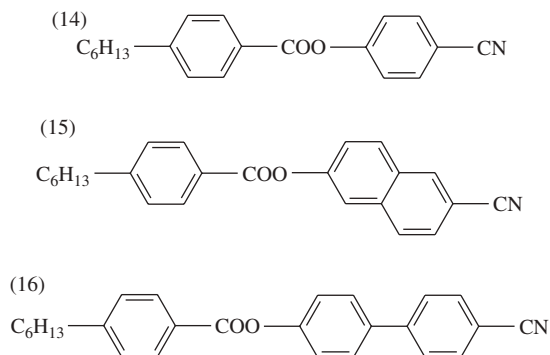
These linkages allow delocalization of electron density between the terminal aromatic rings, and have the effect of retaining the rigidity and planarity of the central core. The delocalized electron density can enhance the molecules anisotropic polarizability. Interestingly, the analogue of the above molecule in which the two aromatic rings are joined by a double bonded rather than a triple bond does not necessarily form a liquid crystal phase. The *trans* isomer retains the overall linear profile and can form a liquid crystalline phase whereas the *cis* does not.^{18,19}



The importance of the effect of the length of the central rigid core of the structure on the thermal stability is illustrated by the following comparison:

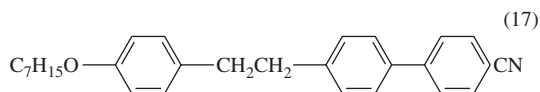


Molecule **(12)** exhibits transitions C–N at 148 °C and N–I at 143 °C, whereas **(13)** has transitions C–N at 172 °C and N–I at 199 °C. Replacement of a single *p*-phenylene ring by a 4,4'-biphenyl or 2,6-naphthalene ring system strongly increases the N–I temperature as illustrated in the following compounds:¹⁶



The respective transitions for **(14)** are C–N at 44.5 °C and N–I at 47 °C; for **(15)** are C–N at 72.8 °C and N–I at 138.4 °C; and for **(16)** are C–N at 91 °C and N–I at 229.6 °C. These examples emphasize the importance of extending the rigid core structure. The more elongated the molecule the greater the anisotropic polarizability and conversely changing the conjugated linking units to their flexible saturated equivalents, such as $-\text{CH}_2\text{CH}_2-$, $-\text{OCH}_2\text{CH}_2\text{O}-$ or $-\text{CH}_2\text{O}-$, usually

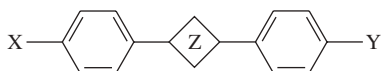
leads to non-liquid crystalline materials or to *mesogens* with phases that have a lower thermal persistence. Even when three rings are involved and two are directly linked or are linked by a unit that preserves conjugation and molecular rigidity, a second linking unit can be more flexible and the resultant *nematic* phases are reasonably thermally persistent. If a considerable proportion of a lath-like molecule is rigid then it can pack parallel to neighbouring molecules and the more flexible groups become constrained to be in line with more rigid parts.¹⁷



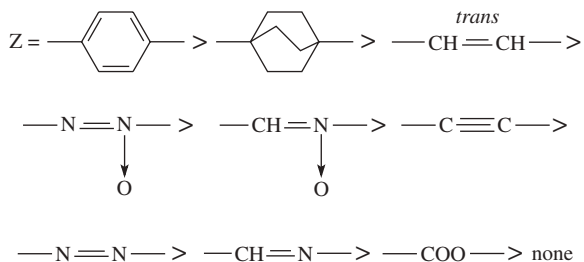
Molecule (17) despite containing a flexible linkage exhibits $C \rightarrow S_A$ at 61.3 °C, $S_A \rightarrow N$ at 125.8 °C and $N \rightarrow I$ at 147.8 °C. A plot of the $N \rightarrow I$ transition temperatures for mixtures of compound (10) with compound (17) is a curve rather than the normal linear plot found with binary mixtures. For compositions around the 50% region the $N \rightarrow I$ temperature is considerably higher than would be expected. This can be explained if we assume that in the pure compound (17) the breakdown of the *nematic* order is due to the onset of rotations about the CH_2-CH_2 link as the temperature is increased. At the lower $N \rightarrow I$ temperature of the mixtures, these rotations may be less important and compound (17) behaves as if it has a more rigid structure with a higher $N \rightarrow I$ temperature, probably around 180 °C. Such an $N \rightarrow I$ value would be more characteristic of a compound with three *p*-phenylene rings in a rigid molecule, e.g. 4''-substituted 4-cyano-*p*-terphenyl (11).¹⁰

3.3.2 Influence of the Linking Group on the Thermal Stability of the Nematic Phase

If we consider molecules with the general structure

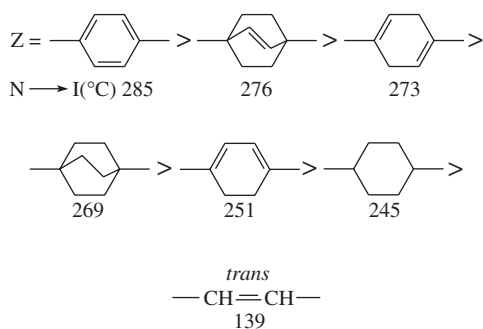


with minor exceptions dependent upon the nature of the end groups X and Y, it is found that the following order is observed in terms of stability of the $N \rightarrow I$ transition:



Stable *mesophases* are produced by substituted *p*-terphenyls and *trans*-stilbenes, whereas *mesophases* of lower thermal stability are formed by Schiff bases,²⁰ esters and biphenyls. Stereochemical considerations are important and affect the position in the order, e.g. stilbenes are planar, azoxybenzenes are slightly twisted and Schiff bases are considerably twisted. The relatively low position of the tolanes ($Z=-C\equiv C-$) in the order is surprising since crystalline diphenylacetylene²¹ contains planar molecules and possibly in the mesophase the rings become non-coplanar. The consequences, however, could be less serious than those in Schiff bases, since the cylinder of electron density associated with the molecular orbital of the $-C\equiv C-$ linkage may still allow conjugation to occur even when the rings are non-coplanar.

The high position of the bicyclic octane ring²² reflects both its rigidity and also cylindrical characteristics. In a related set of molecules it has been found that



indicating that rings are much more effective than a stilbene linkage. The bicyclic octene ring is a little more effective than the bicyclic octane ring so that unsaturated linkages are of significance, although obviously not the only factor. This is also shown by the superiority of the two cyclohexadiene rings over the cyclohexane ring; one would anticipate that the cyclohexa-1,3-diene ring would have been superior to the cyclohexa-1,4-diene since the former should permit extended conjugation within the molecule. However, the butadiene system is quite seriously twisted in the ring structure and this unquestionably lowers the position of the cyclohexan-1,3-diene ring in the order. These results again emphasize the importance of a careful assessment of the effect of molecular shape geometry and conjugation on the anisotropic polarizability.^{23,24}

In practice, the rules are complex and it is not correct simply to say that all cyclohexane rings will have the above effects. In the case where the cyclohexane ring is in a terminal function then the reverse effect can be observed. For example the $N \rightarrow I$ transitions in the benzoate esters are lower than those in the corresponding *trans*-cyclohexane carboxylic esters.^{24,25}

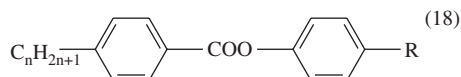
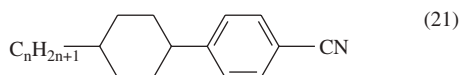
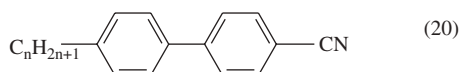
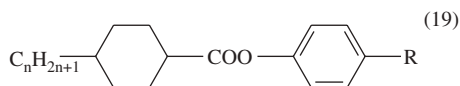


Table 3.3 Transitions for compounds (18), (19), (20) and (21).

18				19			
<i>n</i>	<i>r</i>	<i>C</i> → <i>N</i> (°C)	<i>N</i> → <i>I</i> (°C)	<i>n</i>	<i>R</i>	<i>C</i> → <i>N</i> (°C)	<i>N</i> → <i>I</i> (°C)
5	OC ₄ H ₉	49	58	5	OC ₄ H ₉	49	81
4	CN	67.1	42.6	4	CN	54	67.5
6	C ₅ H ₁₁	28	19	5	C ₅ H ₁₁	36	48

20				21			
<i>n</i>	<i>R</i>	<i>C</i> → <i>N</i> (°C)	<i>N</i> → <i>I</i> (°C)	<i>n</i>	<i>R</i>	<i>C</i> → <i>N</i> (°C)	<i>N</i> → <i>I</i> (°C)
5	CN	22.5	35	5	CN	31	55
6	CN	13.5	27	6	CN	42	47
7	CN	28.5	42	7	CN	30	59

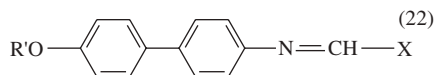


The transitions for the $-\text{OC}_4\text{H}_9$, $-\text{CN}$ and $-\text{C}_5\text{H}_{11}$ forms of compounds (18) and (19) together with those of various alkyl compounds of (20) and (21) are summarized in Table 3.3.

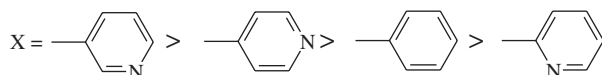
There are obviously subtle effects that influence the precise $\text{N} \rightarrow \text{I}$ temperature, and a number of examples exist of the incorporation of a more flexible cyclohexane ring producing new *mesogenic* compounds, although sometimes it does not.^{26,27}

3.3.3 Terminal Group Effects

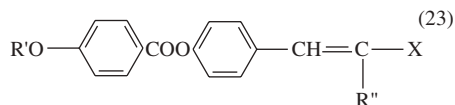
As indicated above, it is possible to create new *mesogens* by changing the terminal group.²⁰ The effectiveness of various groups can change in relation to the core to which they are attached. For instance, consider the following core (22):



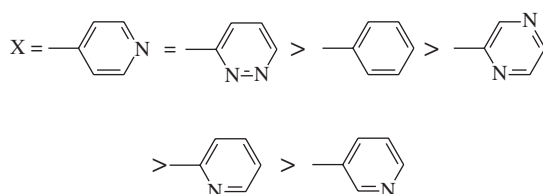
The effectiveness of the terminal groupings can be ranked as:



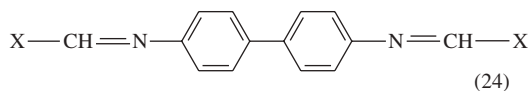
Whereas in compounds with the general formula based on structure (23):



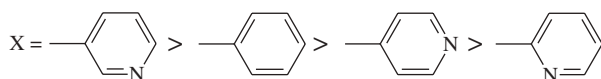
the effective ranking is



In the case of compounds with the general structure typified by (24):



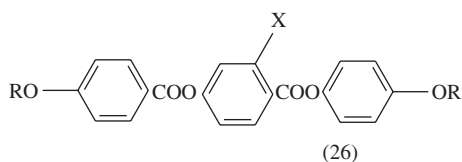
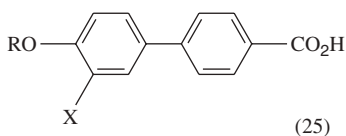
the order now becomes



It is clear that no consistent order exists for the effectiveness of the groupings and careful consideration has to be given to all the possible influences on the force field in predicting the nature of a particular system.²⁰

3.3.4 Pendant Group Effects

Although it is generally accepted that the molecules should be long and rod-shaped, it is also possible to introduce pendant groupings that will disrupt the packing of the molecules and hence extend the *nematic* range. Consider structures of the type (25) and (26):



The $N \rightarrow I$ transition falls in proportion to the size of the substituent in going from $X = F, Cl, Br, I, NO_2, CH_3$.^{26–28} A change in the size of the pendant group leads to a change in the anisotropic polarizability and an increased axial separation of the molecules gives a reduction in the intermolecular attractive forces.²⁸

3.3.5 Terminal Substitution Effects

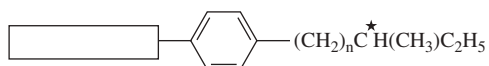
Whilst it is accepted that the shape of a molecule is critical in determining whether the molecule will exhibit *mesogenic* properties, it is the terminal group that often dictates the detailed phase behaviour. The order of terminal group effectiveness in terms of the $N \rightarrow I$ transition is: $Ph > NHCOCH_3 > CN > OCH_3 > NO_2 > Cl > Br > N(CH_3)_2 > CH_3 > F > H$. Replacement of the terminal ring hydrogen in a *mesogen* molecule by any of the commonly encountered substituents will stabilize the *nematic* order. If a *para* substituent can be embedded in the conjugated system, a larger effect is usually observed as a result of its effect on the axial polarizability. Groups that are readily polarizable in general will have a larger effect than those that are not.²⁹

Perhaps the terminal functions which have been of most interest are the alkyl $CH_3(CH_2)_n-$ and alkoxy $CH_3(CH_2)_nO-$ chains. These flexible chains will introduce the disorder that is necessary for the formation of the *nematic* phase.^{30–32} It is generally found that:

- The $N \rightarrow I$ transition temperature alternates in a regular manner, the degree of alternation diminishing as n is increased. This is observed with the melting temperature of the normal alkanes and is attributed to the packing effects of the terminal methyl groups.
- The $N \rightarrow I$ temperature for ethers are in general 30–40 °C higher than those for the corresponding alkyl molecules.
- The $N \rightarrow I$ temperatures for a given series lie on two smooth curves which may either fall or rise as the series is ascended. If the $N \rightarrow I$ temperatures are high, ~ 200 °C, the curves will generally fall; however, if they are low, 20 °C or so, then the curves will rise. The crossover temperature between falling and rising curves would appear to be about 100 °C, in which region the curves are often rather flat.
- For a series of ethers, the even carbon chain members give the upper curve and the odd carbon members the lower curve. This situation is reversed for alkyl chains, where the oxygen in an ether effectively replaces a CH_2 group. This effect is also seen in the crystallization behaviour of polymer chains.
- If the alkyl chain adopts an extended *trans* conformation the axial polarizability increases about twice as much as that at right angles on passing from an even to an odd member of an alkyl substituted series. On passing from an odd to an even number the two polarizabilities increase about equally. At comparable molecular weights, the anisotropic molecular polarizability is therefore greater for odd than for even members and their $N \rightarrow I$ temperatures are higher; the situation is opposite for ethers. This observation implies that there is some conformational preference in the flexible chain.

3.4 Cholesteric Liquid Crystals

Whilst cholesteric liquid crystals, as the name implies, were originally based on cholesterol structures, it is useful to consider the structural features of other molecules that exhibit these phase characteristics.^{33–35} In general, cholesteric *mesogens* are twisted *nematic* phases, but the feature that separates them from other similar molecules is that they possess an asymmetric *chiral* centre. The structural and geometric factors which influence the temperature of the N → I transition are exactly those which influence the other *nematic* liquid crystals. It is usually found that the twisting power of the system diminishes as the chiral centre is moved away from the core structure, *i.e.* as n increases in the structure shown below:



If an oxygen atom replaces a CH_2 group in the flexible chain, the twisting power always decreases. More important, however, is the consistent rule that if the asymmetric centre is S in absolute configuration and the branching point is at an even number of atoms (E) from the core structure, the helix sense will be right handed (D) not left handed (L). We therefore have a simple rule of letters that combine as SED, SOL, REL or ROD, where O refers to a branching point at an odd number of atoms from the core and R refers to the other absolute configuration of the asymmetric centre.^{20,36}

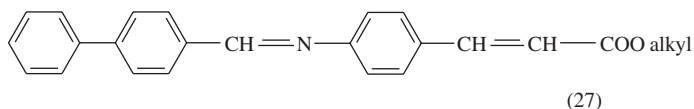
3.5 Smectic Liquid Crystals

There are eight recognized *smectic* types denoted by $S_A, S_B, S_C \dots S_H$. Which phase is formed and the extent of its stability depends very critically upon the nature of the forces which exist between the molecules.³⁷ These forces are very subtle and it is difficult to generalize; however, certain points can be identified which are worth noting.

- (i) If a *smectic* phase is to be formed then the rod-like molecules must usually form a layer crystal lattice that will generate the *smectic* phase on heating. However, even though a suitable molecular arrangement exists in the crystal lattice if the crystal forces are strong and the melting point of the compound is very high, a *smectic* phase may not be observed if the parallel stratified arrangement of the molecules is broken down completely or partially by translation in the direction of the major axis of the molecule. If this occurs then a *nematic* phase can be formed.
- (ii) Replacement of a terminal ring hydrogen in a mesogen by any substituent that does not destroy the linearity of the molecule or broaden it enhances the temperature of the *nematic* to isotropic transition.

However, substituents such as $-\text{CN}$, $-\text{NO}_2$ and $-\text{OCH}_3$ which are high in the nematic terminal group efficiency order are low in the smectic order and can suppress smectic properties relative to nematic phase formation. However, in some instances, e.g. the long-chain 4-*n*-alkyl- and 4-*n*-alkoxy-4'-cyanobiphenyls, the system seems to adapt by forming a S_A phase having an interdigitated bilayer structure and the smectic properties are then enhanced relative to S_H .³⁸⁻⁴⁰ Terminal groups which contribute to the resultant dipole across the long axis, e.g. $-\text{COO}$ -alkyl, $-\text{CH}=\text{CHCO}$ -alkyl, $-\text{CONH}_2$ or $-\text{OCF}_3$, strongly promote smectic properties as do ionized functions, e.g. $-\text{COO}^- \text{M}^+$ or $-\text{NH}_3^+ \text{X}^-$. Groups such as $-\text{Ph}$, $-\text{NHCOCH}_3$ and $-\text{OCOCH}_3$ strongly promote both smectic and nematic properties, but affect the smectic properties more markedly.

- (iii) Extending the length of a terminal *n*-alkyl chain increases the smectic tendencies relative to the nematic tendencies of a system. Eventually a stage is reached when nematic properties are extinguished and the compounds are purely smectic. This behaviour is very general for S_A and S_C phases.
- (iv) Alkyl chain branching on the C_1 of an ester alkyl chain ($-\text{COO}$ -alkyl) has a much smaller effect on the thermal stability of S_A phases than on *nematic* phases. Moving a branching CH_3 to C_2 , C_3 , etc., gives progressively smaller effects. S_B thermal stability is not greatly affected by a methyl branch, but in S_E a 1-methyl group enhances thermal stability. The results in Table 3.4 illustrate the effects observed⁴¹ for compound (27).



- (v) The effects of pendant groups have been studied extensively in system (28) that gives S_C phases when the alkyl chain is sufficiently long. Whereas the *nematic* thermal stabilities decrease in proportion to the size of X, irrespective of its polarity, the $S_C \rightarrow N$ and the $S_C \rightarrow I$ transition temperatures again decrease but do so less in relation to the size of X if X is dipolar. Thus dipole moments do contribute to S_C thermal stabilities. For example, $X = \text{CH}_3$ or Cl has a similar effect in decreasing $T[\text{N} \rightarrow \text{I}]$, but a larger effect on $T[\text{S}_C \rightarrow \text{N}]$ is given by

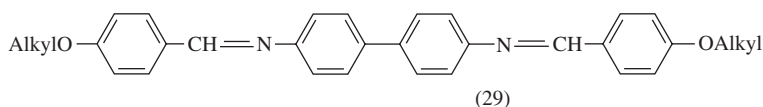
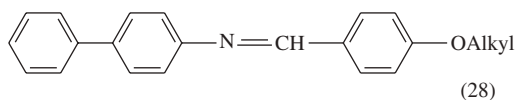
Table 3.4 Transition temperatures for compounds based on compound (27).

Alkyl group	$C \rightarrow S_E$ (°C)	$S_E \rightarrow S_B$ (°C)	$S_B \rightarrow S_A$ (°C)	$S_A \rightarrow I$ (°C)
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	92	101.5	168	204
$\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	70	128	168	180
$\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$	68	113.5	157	190.5
$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	77.5	109	167	196
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	93	108	168	199

$X = \text{CH}_3$. This illustrates the combination of both the effect of size and polarity on the S_C phases.

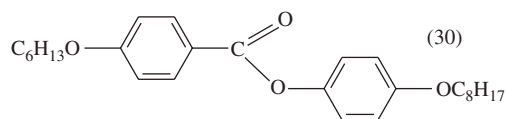
As for *nematic* phases, if the pendant group occupies a recess in the structure such that its full broadening effect is not operative, an increase in S_C thermal stability can arise, e.g. in 5-substituted 6-*n*-alkoxy-2-naphtholic acids. The increase in $T[S_C \rightarrow N]$ is larger than that for $T[N \rightarrow I]$, showing again that dipole interactions play a role in enhancing the thermal stability of the S_C transition.

Schiff bases have been studied in (28) and (29) which exhibit S_A and/or *nematic* phases.⁴²



The 2- and 2'-substituents cause large reductions in $T[N \rightarrow I]$ because of the additional twisting about the inter-ring bond. In the 2-fluoro-substituted compound of (28), $\Delta T[N \rightarrow I]$ is 49 °C. Even larger effects on the S_A phases are observed and $\Delta T[S_A \rightarrow N]$ is 71 °C for the 2-fluoro-substituted compound of (28). Decreases in N and S_A thermal stability of only 0.5 °C and 9 °C, respectively, have been observed for fluoro substituents that exert no steric effect.⁴² Unlike the trends in $T[N \rightarrow I]$ which follow the substituent size, the trends in $T[S_A \rightarrow N]$ are irregular, suggesting that dipolar effects could again be playing a role.

- (vi) Finally, in assessing a situation with regard to *smectic* or *nematic* tendencies, attention has to be paid to the location in the molecule of particular functions. For example, whereas a terminal COO-alkyl group favours *smectic* properties, the -COO group may be used successfully to link ring systems and produce strongly *nematic* materials. An illustration of this behaviour is benzoate esters such as (30) which are purely *nematic* ($C \rightarrow N$ occurs at 54 °C; $N \rightarrow I$ occurs at 89 °C despite the long alkyl chains at each end).



It is only possible in this chapter to outline briefly some of the factors that influence the formation of liquid crystalline phases and influence their stability, but these illustrations indicate how subtle effects of steric and dipolar interactions combine to give a large range of compounds which exhibit liquid crystalline behaviour. A more extensive discussion can be found elsewhere.²⁰

3.6 Theoretical Models for Liquid Crystals

The general rules that emerge from analysis of the factors that influence the formation of a liquid crystalline phase are that:

- the molecules should contain a significant rigid block plus a flexible element which introduces the required level of disorder to avoid crystallization of the molecules,
- the length to the breadth of the molecules is usually of the order of 6 : 1, and
- the molecules in general will contain an element of the structure which is capable of significant long-range dipolar interactions.

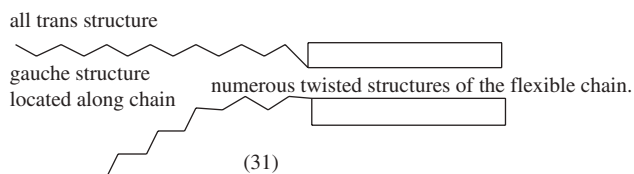
Theoretical interest over the last thirty years in the modelling of the properties of liquid crystals has been driven by their application in displays. A variety of theoretical approaches have been applied to the description of the physical properties of liquid crystals. The statistical models developed are intuitively closer to our molecular understanding of these materials and will be considered initially. The more continuum approach, which allows visualization of macroscopic effects, will be considered later.

3.6.1 Statistical Models

If the liquid crystalline molecule is considered as a rod, then as the liquid is cooled and the density increases, the molecules will attempt to align and crystallize. To stop the molecules crystallizing it is necessary for the alignment of individual pairs of molecules to be inhibited. A molecule in the isotropic liquid phase has three degrees of freedom: two degrees of freedom in terms of rotation about the major and minor axes and one in terms of translation. Loss of these elements of freedom describes the liquid crystal phase transitions discussed above.

Starting from the isotropic phase, where the molecules have all three degrees of freedom, cooling will increase the density and rotation about the long axis becomes restricted. Series of models have been developed that consider the density of liquid in terms of the restriction of the order.⁴³⁻⁴⁷ These theories identify a critical density at which the isotropic to *nematic* transition would be predicted. Constraint of the molecule in terms of its rotation about the long axis defines the *nematic* phase. If now the translational freedom is restricted and layered alignment is imposed on the molecules, then *smectic* order is created. The *smectic* phase can still retain disorder in rotational freedom about the short axis. Loss of this final degree of freedom will lead to the creation of a crystalline ordered structure. This simple approach provides a description for the isotropic \rightarrow *nematic* \rightarrow *smectic* \rightarrow crystalline transitions.

Many molecules exhibiting liquid crystal properties have either a terminal alkyl or alkyl ether group. The terminal chains exhibit a number of different conformations, as in (31):



Within the liquid crystalline phase at a defined temperature there will be a statistical distribution of molecules with different chain conformations. As the liquid is cooled, so the lower energy *all-trans* conformation becomes preferred. There is a tendency for molecules with a similar structure to cluster and form nuclei for crystallization. Disordered clusters, however, form the basis of liquid crystalline phases, alignment being restricted to a preferred direction. The alignment of the molecules in space will not necessarily be continuous throughout the bulk of the material as would be found in a crystal. The variation of the direction of the molecular alignment can change in space in addition to the local order varying in the way that is broadly defined by the classification of *nematic* or *smectic* structures. The possible complexities of such a structure have led to the requirement to consider the nature of the organization in terms of an 'order' parameter.

The problem with the accurate modelling of the strength of the potential field that acts on a molecule depends on the type of model used. Most models use the van der Waals potential to describe the strong interactions between neighbouring molecules. In the calculation of the force field, it is usual to consider an average of six nearest neighbours. This approach immediately introduces the concept that the potential energy function should be a *mean field approximation* being an average of the interaction between specific elements of the molecular structure. A molecule in the *nematic* phase may be assured to have a higher degree of rotational freedom about its long axis than in a crystal and therefore it is reasonable to assume that a *mean field potential* is appropriate for the modelling of this type of situation. As will be appreciated from the above discussion of the molecular structure, most liquid crystalline materials will contain a significant dipole or anisotropic electronic polarizability. The dipolar and higher order anisotropic electronic polarizability effects are longer-range effects. The asymmetry of the force field will ultimately remove the rotational degree of freedom about the long axis, assist the alignment of molecules into layered structures and ultimately create the organization found in crystals. A refined model would consider the rod as being made up of a rigid element that contains dipole/electronic interaction and the flexible tail element that introduces the entropic element that helps create a variety of twisted and bent morphologies which are found in liquid crystals and helps suppress the formation of ordered crystalline material. This simple approach alters the description of the system in terms of a series of partition functions and allows a statistical mechanical approach to be developed for the description of the liquid crystalline phase.

3.6.2 Development of Statistical Mechanical Models

The first statistical theory was developed considering the critical density for the formation of the *nematic* phase and was based on a simple mean field approximation of the description of the force field.⁴³⁻⁴⁵ This study leads to predictions that there should be a critical density ρ^* at which the phase transition will occur. Since on cooling the material the density will increase, there will also exist a critical temperature T^* at which such a transition occurs.

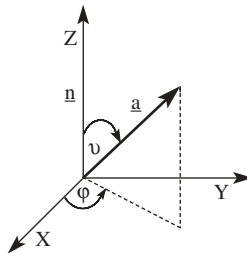
3.6.3 Distributions and Order Parameters

Using birefringence to examine the molecular alignment in a typical *nematic* indicates that there is a spread of orientations about the general direction of alignment. As a result there is an angle θ_1 between the applied field and the average direction of alignment of the molecules θ_2 . The molecules will be distributed around this latter angle and expressed by the second Legendre polynomial [P_2], which automatically ignores higher order moments and hence assumes rotational averaging.

In an isotropic medium, the value of a physical property can be represented by a scalar quantity; however, for an anisotropic medium the value depends on the measuring angle relative to the direction of alignment designated as the *director*. The properties of a *nematic* must be represented by a tensor which in the case of a uniaxial *nematic* for a property X can be conventionally expressed by $X_1=X_2=X_\perp$ and $X_3=X_\parallel$ which are, respectively, the values of the property X perpendicular and parallel to the director:

$$\mathbf{X} = \begin{bmatrix} X_1 & 0 & 0 \\ 0 & X_2 & 0 \\ 0 & 0 & X_3 \end{bmatrix} \quad (3.1)$$

we consider the molecule to resemble a rigid rod and select the optical axis by defining a unit vector \mathbf{a} in the laboratory frame and give it an angle ν to the *director*, where \mathbf{n} lies along the Z-axis and ϕ is the angle formed between the projection of \mathbf{a} onto the X-Y plane and the X axis:



The components of the vector \mathbf{a} are

$$a_z = \cos \nu; \quad a_x = \sin \nu \cos \phi; \quad a_y = \sin \nu \sin \phi \quad (3.2)$$

A distribution function $f(v, \varphi)d\Omega$ can be defined which gives the probability of finding rods in a small solid angle $d\Omega = \sin v \, dv d\varphi$ around the direction (v, φ) . As \mathbf{n} is defined along the Z-axis, $f(v, \varphi)$ is independent of φ , due to the uniaxial nature of the *nematic*. Consequently \mathbf{n} has complete symmetry around the Z-axis and $\mathbf{n} \cong -\mathbf{n}$; therefore $f(v) = f(-v)$. A straightforward summation would be

$$S_1 = \int \cos v f(v, \varphi) \partial v \partial \varphi = \langle \cos v \rangle = 0 \quad (3.3)$$

This is the second Legendre polynomial. Going to higher order terms gives

$$S_2 = \int \frac{1}{2} (3 \cos^2 v - 1) f(v, \varphi) \partial v \partial \varphi; \quad S_2 = \frac{1}{2} \langle 3 \cos^2 v - 1 \rangle \quad (3.4)$$

The factor of $\frac{1}{2}$ is introduced to avoid double counting of the interactions. This expression is useful, as for a perfectly aligned *nematic* $v=0 \Rightarrow S=1$, whereas in the random or isotropic liquid $\cos^2 v = 1/3 \Rightarrow S=0$. Thus *nematic* liquid crystals have values of S that will range from 0 to 1.

A model for the temperature dependence of the order parameter can be developed based on either assuming that short-range forces are dominant (van der Waals interactions are controlling) or long-range forces are dominant (electrostatic interactions are controlling). The long-range approach has been developed by Maier and Saupe.^{48,49}

This *mean field theory* uses a weak anisotropic potential $F(v)$ which is given the form

$$F(v) = \left(\frac{A}{V^2} \right) S \left(\frac{3}{2} \cos^2 v - 1 \right) \quad (3.5)$$

where A is the strength of the potential and V is the molar volume. The effective orientation potential for a single molecule then becomes

$$U(\cos v) = u_2 S_2 P_2(\cos v) \quad (3.6)$$

Thus the average single particle approximation is proportional to the order parameter squared, where u_2 is related to γ and to T_c , the clearing temperature that marks the nematic to isotropic transition:

$$\gamma = 4.5415 T_c \quad (3.7)$$

This assumes that the van der Waals repulsive forces dominate U_2 , but are perturbed by longer range electrostatic and dipolar interactions and are approximately temperature independent. The Maier–Saupe theory^{48,49} predicts S_2 being a universal function of reduced temperature:

$$\tau = \left(\frac{TV^2}{T_c V_c^2} \right) \quad (3.8)$$

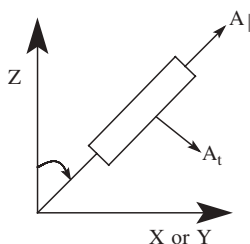
and leads to S_2 being equal to 0.43 at T_c for all materials. At this temperature $(A/VkT) = 4.55$. A reasonably accurate order parameter–temperature relationship is given by the expression

$$S_2 = (1 - 0.98\tau)^{0.22} \quad (3.9)$$

Further refinements of the theory have been made and these lead to more accurate predictions of the behaviour.

The alternative approach of using short-range interactions to create the potential leads to problems with the prediction of the *clearing point*—the *nematic* to isotropic transition. This theory models close packed clustering and hence a pseudo melt transition.

The order parameter is a theoretical tool that can be measured experimentally. It is possible to determine the anisotropy of a particular property for a *nematic* relative to the anisotropy of a perfectly aligned material. Consider a molecule lying at an angle v to \mathbf{n} as indicated below:



The value of a particular property along the molecular axis is A_l and the value along the ordinary axis is A_t and correspond to the values which would be obtained from studies of a perfect single crystal. Thus the property A can be expressed as

$$\mathbf{A} = \begin{bmatrix} A_t & 0 & 0 \\ 0 & A_t & 0 \\ 0 & 0 & A_l \end{bmatrix} \quad (3.10)$$

Thus the effective value of the property A along the Z-axis will given by

$$A_z = A_l \cos^2 v + A_t \sin^2 v \quad (3.11)$$

$$= A_l \cos^2 v + A_t \sin^2 u \quad (3.12)$$

$$= (A_l - A_t) \cos^2 v + A_t \quad (3.13)$$

$$= \frac{(A_l + 2A_t)}{3} + \frac{2}{3}(A_l - A_t) \frac{(3 \cos^2 v - 1)}{2} \quad (3.14)$$

$$= A_{\text{iso}} + \frac{2}{3}(A_l - A_t) \left(\frac{3 \cos^2 v - 1}{2} \right) \quad (3.15)$$

where A_{iso} is the isotropic or average value of the property A . Summing over all molecules:

$$A_{\parallel} = A_{\text{iso}} + \frac{2}{3}(A_{\parallel} - A_{\perp}) \left\langle \frac{3 \cos^2 v - 1}{2} \right\rangle \quad (3.16)$$

However

$$S_2 = \frac{1}{2} \langle 3 \cos^2 v - 1 \rangle \quad (3.17)$$

so that

$$S_2 = \frac{3 A_{\parallel} - A_{\text{iso}}}{2(A_{\parallel} - A_{\perp})} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} - A_{\perp}} \quad (3.18)$$

It is therefore possible if the single crystal property is known to determine the order parameter of the liquid crystalline phase.

3.7 Elastic Behaviour of Nematic Liquid Crystals

The *nematic* phase has properties that resemble those of a solid yet also those of a fluid. A very successful approach to modelling the behaviour of liquid crystals is based on fluid dynamics. These theories are based on the concept of the Leslie–Erickson theory of hydrodynamic flow.^{50,51} The theory considers the use of a series of coefficients, the rotations between the coefficients describing the liquid. The state of a fluid at point \mathbf{r} where $\mathbf{r} = (x, y, z)$ at a given time is defined by the fluid velocity $\mathbf{v}(\mathbf{r}, t)$ and any two thermodynamic variables, such as pressure $P(\mathbf{r}, t)$ or density $\rho(\mathbf{r}, t)$. The fluid obeys the conservation laws:

- *Conservation of mass.* Consider a surface of unit area, through which a fluid flows. In a unit time, the mass of fluid that flows through that area is the component of $\rho \mathbf{v}$ normal to that area. The variation of $\rho \mathbf{v}$ is the rate of change of the density per unit time so that: $(\partial \rho / \partial t) + \Delta(\rho \mathbf{v}) = 0$.
- *Conservation of linear momentum.* The rate of change of momentum of a volume element in the fluid is equivalent to the total force \mathbf{F}^T acting on the element $\mathbf{F}^T = \rho(\partial \mathbf{v} / \partial t)$ and the acceleration is given by $\partial v_i / \partial t = (\partial v_i / \partial t) + v_j(\partial v_i / \partial x_j)$. The possible contributions to \mathbf{F}^T may come from pressure P , viscous drag \mathbf{F}^v or an external field \mathbf{F}^f which could be gravitational, electrical or magnetic: $\rho(\partial \mathbf{v} / \partial t) = \mathbf{F}^v + \mathbf{F}^f - \Delta P$. The force per unit area \mathbf{t} acting on a normal to a surface v is given by $t_i = t_{ij} v_j$. The components of t_{ij} represent the i th component of force on a surface and x_j equals a constant. Where $i = j$, this is equivalent to a compression and where $i \neq j$, these are shear stresses. Consequently t_{ij} can be split into parts for an incompressible fluid: $t_{ij} = -P \delta_{ij} + \hat{t}_{ij}$, where \hat{t}_{ij} is the extra stress tensor and δ_{ij} is the Kronecker delta. The conservation of linear momentum now takes the form $\rho(\partial v_i / \partial t) = F_i - P_i + \hat{t}_{ij,j}$. In the case of a transverse velocity gradient $\partial u / \partial x$, the induced shear stress in flow becomes $\hat{t}_{21} = \eta(\partial u / \partial x)$, where η is the viscosity coefficient. In the general

form $\hat{t}_{ij} = \eta[(\partial v_i/\partial x_j) + (\partial v_j/\partial x_i)]$, where $\partial u_i/\partial x_j$ is the transpose of $\partial u_j/\partial x_i$. It can be shown that every tensor can be split into a symmetric and an asymmetric part. Carrying out this operation on the viscosity gradient tensor, the symmetric part is

$$A_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) = \frac{1}{2} (v_{i,j} + v_{j,i})$$

and the anti-symmetric part is

$$\omega_{ij} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i} \right) = \frac{1}{2} (v_{i,j} - v_{j,i})$$

Thus A_{ij} is the stretching tensor or rate of strain and ω_{ij} is the rotation or vorticity tensor and are illustrated below.

- *Conservation of angular momentum.* The net torque about a given point which acts on the particle is a volume V , relating to the body forces acting throughout the volume and the stress acting on the surface. Consequently at least force couples may also act on the material and are characterized by the vector K_i , force per unit mass. Although force couples are generally not considered in hydrodynamics, they are important in this context as they allow the introduction of external forces: magnetic and electric fields, *etc.* By equating the net torque about a point with the rate of change of angular momentum and assuming that there are no stress couples, it can be shown that $\epsilon_{ijk} t_{kj} + K_i = 0$. This illustrates that when there is no force couple acting throughout the fluid ($K_i = 0$) the stress tensor is symmetric.
- *Conservation of energy.* The conservation of energy is the equivalence of the material derivative of kinetic and internal energy with the rate at which mechanical work is done on the fluid. Thus work is concerned with the effects of external forces producing kinetic energy and viscous dissipation. If the rate of viscous dissipation is $\rho \dot{\Phi}$ then $\rho \dot{\Phi} = \hat{t}_{ij} v_{ij}$, and since the stress is symmetrical the above expression becomes $\rho \dot{\Phi} = \hat{t}_{ij} A_{ij} = 2\eta A_{ij} A_{ji}$ and the rate of increase of entropy \dot{S} is equivalent to the heat supply divided by the temperature: $\dot{S} = (1/T) 2\eta A_{ij} A_{ji}$. As \dot{S} is positive, so the coefficient of the viscosity must be positive.

The above is a quick summary of the relevant hydrodynamic equations for a simple fluid. The behaviour of a *nematic* liquid crystal is more complex in that the stress tensor is now non-symmetric. Another variable that is introduced is the director, \mathbf{n} , defined by a unit vector, where $\mathbf{n} \sim -\mathbf{n}$. Allied to these constraints, one defines the rate of rotation of the director with respect to the background fluid by

$$N_i = \dot{n}_i - \omega_{ij} n_j \quad (3.19)$$

Applying the conservation laws summarized above gives

$$\text{Conservation of mass : } v_{i,i} = 0 \quad (3.20)$$

$$\text{Conservation of linear momentum : } \rho \dot{v}_i = \rho F_i + t_{ij,i} \quad (3.21)$$

$$\text{Conservation of angular momentum : } o \varepsilon_{ijk} n_j \dot{n}_k = K_i + \varepsilon_{ijk} t_{kj} + l_{ij,j} \quad (3.22)$$

$$\text{Conservation of energy : } \dot{E} = t_{ij} v_{i,j} + s_{ij} (\dot{n}_i)_j - g_i n_i \quad (3.23)$$

where o is an internal constant associated with the director. This term is taken as being equal to a^2 , where a is a molecular dimension. Since this is a constant it is often ignored. F is the external body force, K is the external body couple, t is the stress couple tensor, E is the internal energy per unit volume, s is the director stress tensor and g is the intrinsic *director* body force. The constitutive equations are^{50,51}

$$t_{ij} = -P \delta_{ij} - \frac{\partial W}{\partial n_{k,j}} n_{k,i} + \tilde{t}_{ij} \quad (3.24)$$

$$s_{ij} = n_i \beta_j + \frac{\partial W}{\partial n_{i,j}} + \tilde{s}_{ij} \quad (3.25)$$

$$g_i = \lambda n_i - (n_i \beta_j)_j - \frac{\partial W}{\partial n_i} + \tilde{g}_i \quad (3.26)$$

where W is the free energy density relating to the elastic energy deformation, \tilde{t}_{ij} is the viscous stress tensor, β is an arbitrary vector arising from the constrained director, ($n_i n_i = 1$), \tilde{g}_i is the intrinsic director body extra force and \tilde{s}_{ij} is the director extra stress tensor, which equals zero. These extra terms relate to the dynamic behaviour of the system. The above equations lead to

$$\tilde{t}_{ij} = \alpha_1 n_k n_p A_{kp} n_i n_j + \alpha_2 n_i n_j + \alpha_3 n_j n_i + \alpha_4 A_{ij} + \alpha_5 A_{ik} n_k n_j + \alpha_6 A_{jk} n_k n_i \quad (3.27)$$

where $\gamma_1 = \alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_6 - \alpha_5$ and α_i are the Leslie coefficients of the viscosity. Leslie has subsequently shown that these coefficients are related to the various components of the viscosity. The coefficient α_4 is the isotropic viscosity coefficient and does not involve the director. The coefficients α_1 , α_4 , α_5 and α_6 are related to the deformation tensor, whereas α_2 and α_3 involve only the vorticity and are related to the coupling between the director orientation and the flow.

The above equations can be related to measurable viscosity coefficients. The coefficients allow one to develop the concepts of stability of the flow in the applied field and have allowed examination of the dynamics of switching of the liquid crystal systems. The above theory illustrates that although the liquid crystals have many facets of liquids they exhibit coupled behaviour that is characteristic of solids.

3.8 Computer Simulations

Paralleling the developments of liquids, considerable interest has been shown in the ability to develop computer-based theoretical models that can describe the onset of the *mesophase*. As might be expected, much of the modelling is based on a Monte Carlo or a molecular dynamics approach. Zannoni⁵² has reviewed some of the earlier simulations. The Monte Carlo approach involves the orientation of the molecules being determined by an averaged potential function and using the Metropolis technique,⁵³ which involves introducing a stochastic process in that asymptotically each configuration recurs with a frequency proportional to the Boltzmann factor for that state. In order to achieve calculations that describe the whole system it is usual not to impose boundary conditions and use the technique of periodic boundaries to simulate bulk behaviour. In the usual application, it is known that surface interactions are critically important and hence the simulation of these effects is particularly taxing in terms of computer time. To assist with the scaling of the calculations it is also appropriate to compute the orientational order parameter to assess the degree and type of alignment being created. Lattice models based on the density correlations have also been widely reported and demonstrate good qualitative correlation with experiment. The molecular dynamics simulations involve setting up and solving numerically the equations of motion for a system of N molecules contained in a box of given volume. The calculations involve the separation of rotational and translational motion and examination of the contribution each makes to the total energy.

Recent simulations work⁵⁴ has demonstrated the Gay–Berne (GB) potential,⁵⁵ developed more than twenty years ago as a model for describing the interactions between two elongated rigid molecules, provides a very useful approach to liquid crystal modelling. The GB potential owes much to the pioneering work of Corner⁵⁶ who noted that the Lennard-Jones 12–6 potential provided a good description of the potential between a pair of atoms and so could also be used to describe the interactions between larger molecules if their deviations from spherical symmetry were coded into the potential. Although his ideas worked reasonably well for small molecules such as the nitrogen dimer, the potentials were not suitable for more elongated molecules, especially those of length-to-breadth ratios characteristic of liquid crystals.

Gay and Berne⁵⁵ showed that the interaction potential between a pair of rigid, elongated molecules could be reasonably well represented in a Lennard-Jones 12–6 form by

$$U(\text{GB})(\hat{u}_i, \hat{u}_j, r) = 4\epsilon(\hat{u}_i, \hat{u}_j, r) \left[\frac{\sigma_s}{r - \sigma(\hat{u}_i, \hat{u}_j, \hat{r}) + \sigma_s} \right]^{12} - \left[\frac{\sigma_s}{r - \sigma(\hat{u}_i, \hat{u}_j, \hat{r}) + \sigma_s} \right]^6 \quad (3.28)$$

where \hat{u}_i and \hat{u}_j are unit vectors describing the orientations of the two molecules and \hat{r} is a unit vector along the intermolecular vector r , with $r = |r|$. Unlike the

scalar s in the well-known Lennard-Jones potential for atoms, the distance parameter $\sigma(\hat{u}_i, \hat{u}_j, \hat{r})$ for elongated molecules should be dependent on the orientations of the two molecules and the intermolecular vector.⁵⁷ This is written as

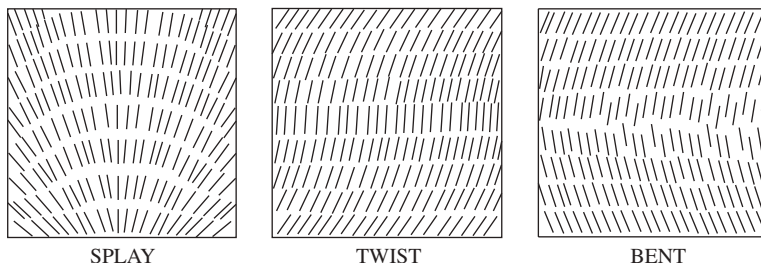
$$\sigma(\hat{u}_i, \hat{u}_j, \hat{r}) = \sigma_s \left[1 - \frac{\chi}{2} \left(\frac{(\hat{u}_i \hat{r} + \hat{u}_j \hat{r})^2}{1 + \chi(\hat{u}_i \hat{u}_j)} \right) + \frac{(\hat{u}_i \hat{r} - \hat{u}_j \hat{r})^2}{1 + \chi(\hat{u}_i \hat{u}_j)} \right]^{-1/2} \quad (3.29)$$

Although this looks complicated, it is just a way of coding the shape of the molecule into the orientation-dependent contact separation. A key component of the potential is the anisotropy in the shape of the molecule, χ , which is dependent on the length-to-breath ratio, κ ($= \sigma_e/\sigma_s$, where σ_e and σ_s are, respectively, the length and breadth of the molecule), and defined by $\chi = (\kappa^2 - 1)/(\kappa^2 + 1)$. Similarly, the energy parameter $\varepsilon(\hat{u}_i, \hat{u}_j, \hat{r})$ should also be orientation dependent.⁵⁶ An important parameter entering this term is the ratio of the potential energy for a pair of molecules in the side-by-side arrangement to that in the end-to-end arrangement: $\kappa' = \varepsilon_s/\varepsilon_e$. Two further parameters are included, m and n , allowing some extra freedom for the potential to be fitted to a particular model. Using this approach, fairly accurate estimates of the temperature of the transitions have been obtained; however, some of the more detailed predictions tend to be less accurate.

3.9 Defects, Dislocations and Disclinations^{20,58}

Whereas defects in molecular crystals are associated with dislocations, in liquid crystalline materials disclinations are discontinuities in orientation in the bulk material, *i.e.* within the *director* field. Disclinations are line singularities perpendicular to the layer. They appear as dark brushes when thin films (10 μm) are viewed under cross polarizers. On rotating the polarizers, the positions of the points remain unchanged but the brushes themselves rotate continuously. The sense of the rotation may either be the same sense as that of the polarizers (positive disclinations) or opposite (negative disclinations). The rate of rotation is about equal to that of the polarizers when the disclination has four brushes and is twice as fast when it has only two. The strength of the disclination is defined as $S = (\text{number of brushes})/4$. A number of these structures have been observed, $S = +1/2, -1/2, +1$ and -1 . Neighbouring disclinations connected by brushes are of opposite signs and the sum of the strengths of all disclinations in the sample tends to zero. Normally, disclinations remain static in the field of view but as the temperature approaches the nematic–isotropic transition they tend to become mobile and disclinations of opposite sign are seen to attract one another and coalesce.

To understand the relationship to the director it is helpful to consider a planar sample in which the director orientation is parallel to the glass surfaces and not a function of the thickness. This assumption is of course not valid close to the singularities. We will firstly consider *nematic* liquid crystals with a curved structure, splay, twist and bend, as indicated below:



The elastic free energy per unit volume is $\frac{1}{2}k_{11}(\partial\phi/\partial x)^2$, where $\phi = n_x$ is the tilt of the *director* and k_{11} the splay constant. The free energy density may be written for splay as $F = \frac{1}{2}k_{11}(\partial n_x/\partial x)^2$, for twist as $F = \frac{1}{2}k_{22}(\partial n_x/\partial y)^2$ and for bend as $F = \frac{1}{2}k_{33}(\partial n_x/\partial z)^2$. In the more general form it may be written as

$$F = \frac{1}{2}k_{11}(\nabla\mathbf{n})^2 + \frac{1}{2}k_{22}(\mathbf{n}\nabla\times\mathbf{n})^2 + \frac{1}{2}k_{33}(\mathbf{n}\times\nabla\times\mathbf{n})^2 \quad (3.30)$$

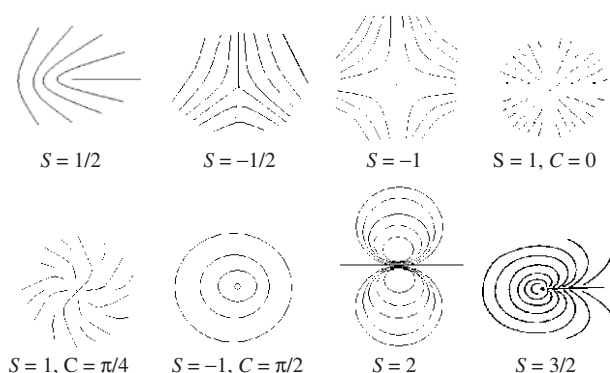
The elastic constants k_{11} , k_{22} and k_{33} are usually of the order of 10^{-6} to 10^7 dyn.

In the case of the disclinations, only two elastic constants are involved, k_{11} and k_{22} , that to a first approximation are taken as being equal to k . If we consider cylindrical coordinates (r, α) and now seek solutions for eqn (3.30) in which the director orientation ψ is independent of r , then the elastic free energy is

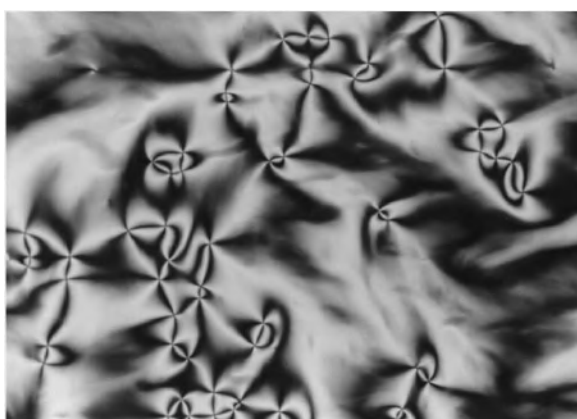
$$F = \frac{1}{2}k \left(\frac{\partial\psi}{\partial\alpha} \right)^2 \quad (3.31)$$

Minimization of eqn (3.31) gives ψ a constant which describes the uniformly orientated nematic sample, or $\psi = s\alpha + c$, where c is a constant. In the nematic case, the orientational order is taken to be polar, and hence $S = \pm 1/2, \pm 1, \pm 3/2, \dots$, with $0 < C < \pi$. The angle between two successive dark brushes is therefore $\Delta\alpha = \Delta\psi/S = \pi/2S$, and thus the number of dark brushes per singularity is $2\pi/\Delta\alpha = 4|S|$. A few examples of the types of molecular orientation in

the neighbourhood of a disclination are shown below:



The curves represent the projection of the *director* field in the xy plane. For $S \neq 1$, a change in C merely causes a rotation of the figure by $C/(1 - S)$, while for $S = 1$ the pattern itself is changed. The disclinations are characterized by their 'strengths', which are defined as the number of multiples of 2π that the director rotates in a complete circuit around the disclination core. A value of $+1$ indicates that the director is rotated through 2π . The micrograph of a liquid crystal material, shown below, illustrates the various disclinations described above.



A variety of optical micrographs of liquid crystal systems are to be found at the following websites:

<http://micro.magnet.fsu.edu/micro/gallery/liqcryst/liquidcrystal.html>

www.cemes.fr/Oper_recherche/Polymer/LCP/Html_LCP/Liquid_Crystals_Physics.htm

www.warwick.ac.uk/fac/sci/Chemistry/jpr/lq/liqcry.html

www.lci.kent.edu/polmmicpic.html

These collections of images illustrate the various types of liquid crystal that have been studied and the broad range of morphologies that can be observed.

3.10 Applications⁵⁹

It is not appropriate to discuss the various ways in which liquid crystals are used, save to say that there are two principal effects that are employed. With chiral nematics the pitch of the rotation of the light will influence the colour that is observed. The interlayer spacing that is itself controlled by the temperature influences the pitch. As a consequence changing the temperature will lead to a change in the colour. This is used in liquid crystal thermometers. Displays, in contrast, use the fact that the alignment of the liquid crystal can be influenced by an external electric or magnetic field. In the case of a twisted nematic the application of an external electric field can change the alignment of the director as viewed through the plane of the liquid crystal film and this will hence change the effects it can have on polarized light. Most optical displays use the fact that liquid crystals can be aligned by interaction with a substrate. As a consequence it is relatively easy to achieve a twisted configuration. Application of an external field can be arranged to rotate the alignment of the liquid crystals so that they will now change their interaction with the polarized light. The results is that colour contrasts can be achieved between those areas where the electric field exists and those where it does not. The reader is referred to specialist texts for a detailed discussion of this topic.⁶⁰⁻⁶⁴

3.11 Polymeric Liquid Crystals

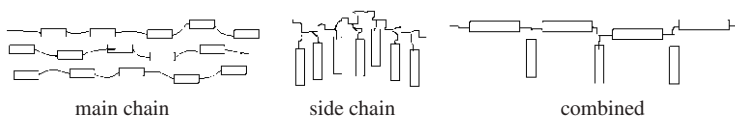
There has been considerable interest in recent years in the study of liquid crystalline order in polymeric materials. Following on from the use of small molecules in display applications, the possibility of creating polymers with similar characteristics became attractive. Onsager⁶⁵ and Flory⁶⁶ predicted that rigid rod-like macromolecules should form liquid crystalline phase. However, it was not until 1975⁶⁷ that the first observation of a thermotropic liquid crystalline polymer was reported. Several reviews have been published on polymeric liquid crystals.⁶⁸⁻⁷⁹

Before examining the properties of polymers which exhibit liquid crystalline characteristics it is appropriate to mention briefly that it is possible to disperse low molecular mass liquid crystals in a polymer matrix and hence achieve an immobilization of the liquid in a solid, yet still achieve many of the desirable optical characteristics of the pure media. These dispersed phases are called *polymer dispersed liquid crystals* and will not be discussed here. These materials, however, are being shown to have many applications and clearly may be technologically important in the future.⁸⁰⁻⁸⁶

3.12 Polymeric Liquid Crystalline Materials

In general, polymeric liquid crystal materials are classified according to the dominant features of their backbone structure into backbone, side chain or

combined liquid crystalline materials:



These characteristic structures can describe most situations found in polymer systems.

3.12.1 General Factors Influencing Polymeric Liquid Crystalline Materials

As would be expected, molecular mass is one of the important factors that will influence the formation of the liquid crystalline phase. Upon increasing the molar mass from a monomer to a polymer, the entropy of the liquid phase (S_i) decreases. The decrease of the entropies of mesomorphic and crystalline phases is less than that of the isotropic phase. The decrease in S_i and that of the liquid crystal phase (S_{lc}) tends asymptotically to zero with increasing molar mass. It follows that the free energies G_i and G_{lc} increase with increasing polymer molecular weight, again becoming asymptotic above a certain molecular weight, and we may consider both parameters as remaining constant. Consider a series of special cases.

Case 1. Both monomeric structural unit and polymer display an enantiotropic mesophase. Upon increasing the molar mass from dimer to trimer, etc., S_i decreases and therefore G_i increases. Beyond a certain molar mass G_i remains for all practical considerations constant. However, the slope of the increase of T_{lc-i} is steeper than that of T_{c-lc} . The difference between these two slopes determines the relative thermodynamic stabilities of the mesomorphic versus the crystalline phases at different polymer molar masses. As the molar mass is increased, the liquid crystalline regime is increased for main chain⁸⁷⁻⁸⁹ and side chain⁹⁰⁻¹⁰⁰ liquid crystalline polymers.

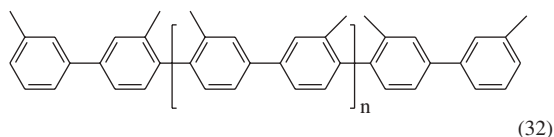
Case 2. The structural unit displays a virtual or a monotropic mesophase; the polymer displays a monotropic or an enantiotropic mesophase. The slope of the T_{lc-c} versus molar mass (M) is steeper than that for T_{c-l} , and as a consequence there will exist a critical value of M below which a mesophase is *not* observed. This effect has been observed in main chain¹⁰¹⁻¹⁰³ and side chain¹⁰⁴ liquid crystalline polymers.

Case 3. The structural unit displays a virtual mesophase; the polymer displays a virtual mesophase. This corresponds to the situation where the slope of T_{lc-c} versus M is greater than that of T_m versus M . The latter lies above the former throughout, and hence the two curves do not cross. Therefore the resulting polymer displays a virtual mesophase. This thermodynamic situation has been observed in polyethers containing both flexible mesogens and flexible spacers.¹⁰⁵

Case 4. Rigid rod-like polymers. The discussion from cases 1 to 3 refers to semi-flexible or semi-rigid and flexible polymer systems that exhibit first-order transition temperatures (*i.e.* melting, isotropic liquid phase) that are molecular mass dependent only up to a certain degree of polymerization. In these systems the melting temperature is determined by the length of the chain fold. Rigid rod-like polymers such as poly(*p*-phenylene)s, poly(*p*-phenylene-benzobisthiazole) (PBT) and poly(*p*-phenylbenzobisoxazole) (PBO) exhibit a linear dependence of their melting transition over the entire range of molar mass.^{106–108} Theory predicts that the axial ratio ($x = L/d$) of rod-like molecules reaches a value of about 6.2, and the compound should exhibit a mesophase. This is the case for poly(*p*-phenylene)s where nematic mesophase behaviour is observed for polymers with a degree of polymerization n between 6 and 7. However, for oligomers with n larger than 7 the nematic phase cannot be observed since the decomposition temperature overlaps the melting temperature and then becomes lower than the melting temperature. Other rigid rod-like polymers such as PBT and PBO and even semi-rigid systems like fully aromatic and unsaturated polyamides and polyesters decompose before melting.

3.12.2 Main Chain Crystalline Polymers

Certain phenyl-linked polymers (32) that exhibit mesophase behaviour will have elements of the structures shown below:^{109–112}

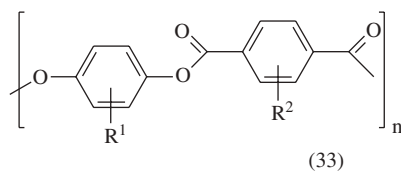


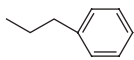
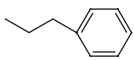
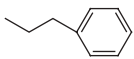
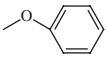
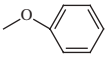
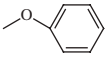
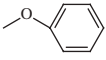

n	Melting temperature ($^{\circ}\text{C}$)	Isotropic–mesophase temperature ($^{\circ}\text{C}$)
1	142	–
2	273	311 (nematic)
3	242	260 (smectic)
4	298	–
5	171	–
6	219	–

These oligomeric methyl-substituted *p*-phenylenes have an axial ratio (x) equal to 0.8 times the number of benzene rings. According to theory predictions hexamethylhexphenyl ($n = 1$) which has $x = 4.8$ and lower oligomers should not exhibit a mesophase, whereas octamethyloctphenyl ($n = 2$) has $x = 6.4$, *i.e.* larger than the critical value of 6.2, and exhibits a nematic phase. A variety of other systems with phenylene structures have been explored; whilst they have

rigid rod-like character, they do not meet the criteria for the breadth to length to make them liquid crystalline.

Substituted polyesters¹¹³ (**33**) as a consequence of the conjugation through the ester function can exhibit the required characteristics of liquid crystalline behaviour.

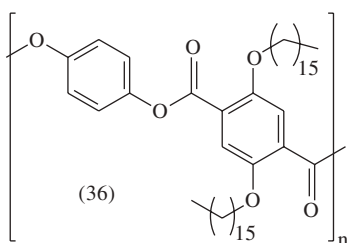
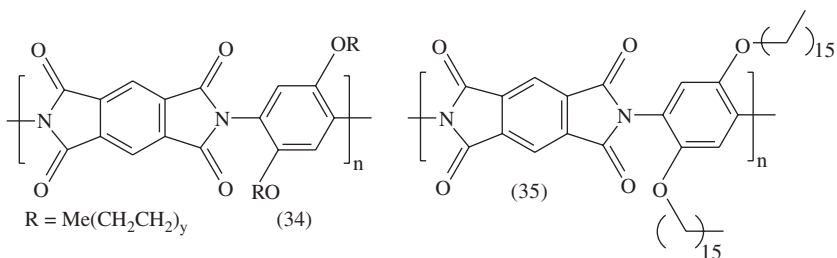


R^1	R^2	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	Mesophase
		60	195	Nematic
Bu ^t		100	225	Nematic
Bu ^t	Br	131	—	—
Bu ^t	CF ₃	141	228	Nematic
	Cl	85	241	Nematic
	Br	90	220	Nematic
	CF ₃	88	—	Isotropic
		112	—	Isotropic

This series of polymers illustrates the breadth to length criteria and demonstrates that only those systems that form a crystalline phase exhibit mesophase behaviour.

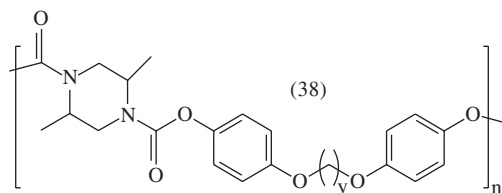
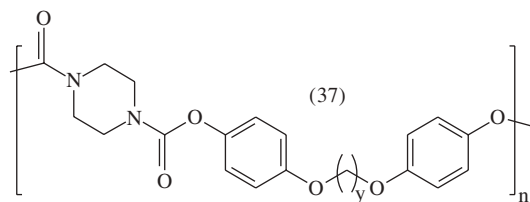
Rod-like soluble polyimides (**34**) have been shown to exhibit liquid crystalline characteristics.¹¹⁴⁻¹¹⁶ All polymers containing alkyl side chains of identical

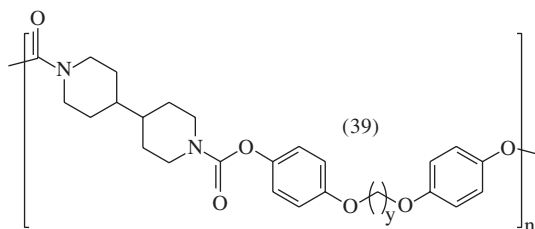
length are isomorphic within their crystalline phase and form solid solutions regardless of the nature of their polymer backbone. For instance (35) is isomorphic with the polyester series (36).¹¹⁶ The rigid rod-like polyimides form layered mesophases.



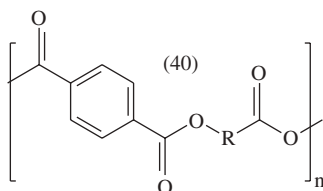
Most of the rigid rod systems form a liquid crystalline phase when cast from a suitable solvent and hence exhibit lyotropic properties.

Polyurethanes with liquid crystalline behaviour have been produced from bischloroformates of 4,4'-alkylenedioxydiphenols by polycondensation with piperazine (37), *trans*-2,5-dimethylpiperazine (38) and 4,4'-bipiperidine (39). These molecules exhibit smectic properties.¹¹⁷⁻¹¹⁹ In general the hydrogen bonding between the neighbouring polymer chains is sufficiently strong to suppress the formation of mesophases; however, some other systems have been reported.¹²⁰



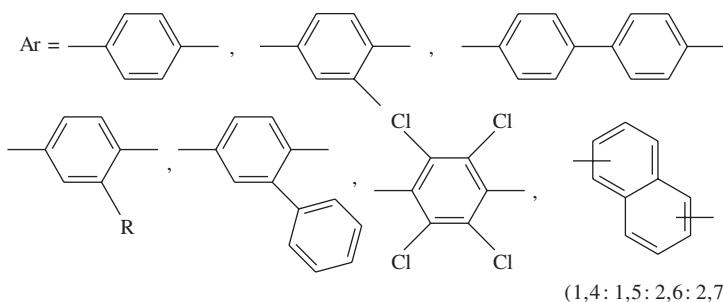
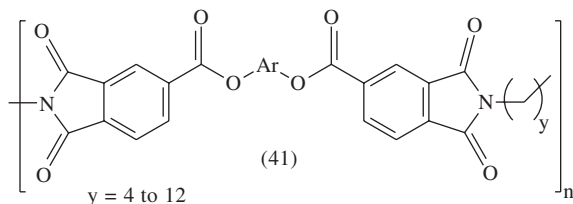


Poly(ester anhydrides) of the type **(40)** exhibit nematic phase behaviour over a broad range of temperatures.¹²¹

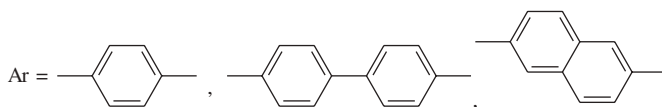
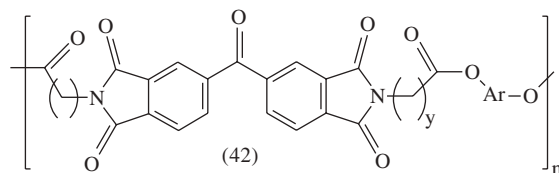


<i>R</i>	T_g ($^{\circ}\text{C}$)	T_i ($^{\circ}\text{C}$)
	136	360
	160	450
	162	440

A number of poly(esterimide)s **(41)** have been shown to exhibit mesophase behaviour. The products of the reaction between trimellitic anhydride and α,ω -diaminoalkanes containing from 4 to 12 methylene units and containing various 4,4' aromatic entities crystallize in a layered morphology but show certain smectic properties.^{122,123} The polymer with Ar = 4,4'-biphenyl melts into a smectic mesophase. The melting point varies from 297 $^{\circ}\text{C}$ for the polymer with $n = 12$ to 393 $^{\circ}\text{C}$ for the polymer with $n = 4$. The liquid crystalline phase becomes an isotropic liquid at 386 $^{\circ}\text{C}$ for the polymer with $n = 12$ and at 467 $^{\circ}\text{C}$ for the polymer with $n = 4$. The rate of crystallization of all these polymers is usually fast with the exception of the polymers based on Ar = 1,4-phenylene, 1,4-tetrachlorophenylene and 2,6-naphthalene that exhibit smectic mesophases; the other polymers melt directly into an isotropic phase.¹²⁴



The reaction of pyromellitic dianhydride or benzophenone-3,3',4,4'-tetracarboxylic anhydride with amino acids or lactams followed by condensation of the resulting diacids with diacetates of hydroquinone, 2,6-dihydroxynaphthalene or 4,4'-dihydroxybiphenyl produced layer polymers (42). With the exception of the polymer with $y=11$, all the polymers based on $\text{Ar}=4,4'$ -biphenyl exhibit a smectic mesophase. The polymer with $y=10$ and $\text{Ar}=1,4$ -phenylene exhibits a smectic mesophase. Polymers based on $\text{Ar}=1,4$ -phenylene or 2,6-naphthalene melt directly into an isotropic phase.¹²⁴



A number of other polymer systems have been shown to exhibit liquid crystal characteristics. In all cases the critical length rule is a very useful guide as to whether such behaviour will be observed. Clearly in these materials, the flexible alkyl element allows the disorder to be created that is the essential feature of liquid crystallinity.

3.12.3 Side Chain Liquid Crystalline Polymers

An extensive study of possible side chain liquid crystalline materials has been undertaken.^{80,125} The majority of materials that have been studied have structures in which a mesogenic low molar mass entity is flexibly attached to a polymer backbone. The usual backbone is a flexible polymer and interestingly small-angle neutron scattering (SANS) experiments^{126–128} and X-ray scattering experiments^{129,130} have shown that the statistical random coil conformation of the polymer backbone is slightly distorted in the nematic phase and highly distorted in the smectic phase.

3.12.4 Nature of Flexible Spacer and Its Length

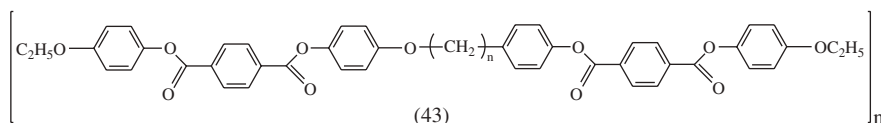
According to the previous discussion it is found that increasing the degree of polymerization decreases the entropy of the system and if the monomeric structural unit exhibits a virtual or monotropic or mesophase, the resulting polymer should most probably exhibit a monotropic or mesophase. Alternatively, if the monomeric structural unit displays a mesophase, the polymer should display a mesophase that is broader. It is also possible that the structural unit of the polymer exhibits more than one virtual mesophase and therefore at high molecular weights the polymer will increase the number of its mesophases. All these effects have been observed in various systems.¹³¹

The length of the flexible spacer determines the nature of the mesophase. Long spacers favour smectic phases while short spacers favour nematic phases. This effect is similar to that observed in low molar mass liquid crystals.

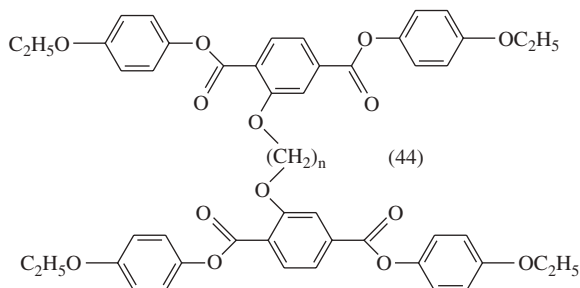
3.12.5 Nature of the Backbone

At constant molecular weight the rigidity of the polymer backbone determines the thermodynamic stability of the mesophase. Accordingly a polymer with a more rigid backbone should have a more stable mesophase. However, the experimental situation is reversed and is explained by assuming that a more flexible backbone uses less energy to get distorted and therefore generates a more decoupled polymer system. In fact, the more flexible backbones do not only generate higher isotropic temperatures but also greater ability towards crystallization. However, contrary to all expectations the entropy change of the isotropic transition is higher for these polymers that are based on more rigid backbones and therefore they exhibit lower isotropic temperatures. This contradiction between the values of the entropy change and the isotropic temperatures can be accounted for by a different mechanism of distortion of the polymer backbone. In the case of a flexible chain the backbone can become sandwiched between the smectic layers, whereas in a less flexible system the chains have to weave in and out of the liquid crystalline layers. Hence the difference observed reflects the ability of the backbone and side chains to accommodate each other in the compacted matrix. There will always be a

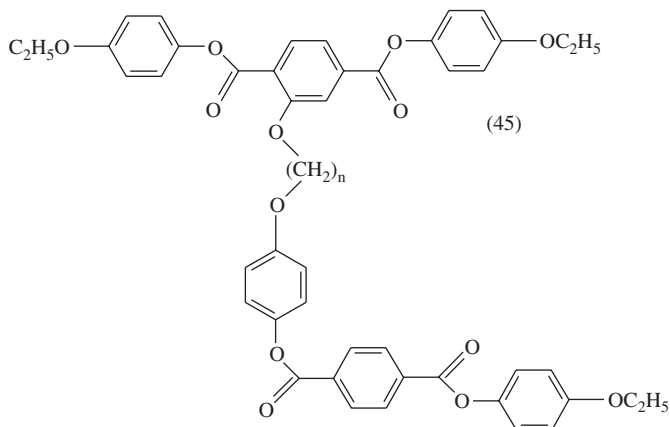
driving force for the elements to phase separate and microphase separation has been reported in a number of systems. The molar mass at which the isotropic temperature becomes independent of molar mass depends on the flexibility of the polymer backbone; the temperature for the polysiloxanes^{132,133} is higher than that for poly(methyl acrylates).¹³³ As pointed out recently,¹³⁴ for monomers, based on the ability to form mesophases, it is possible to predict whether they will form mesophase polymer systems. The vast majority of liquid crystal dimers studied consist of two identical rod-like mesogenic units linked in terminal positions via a flexible alkyl chain normally containing between 3 and 12 methylene units.¹³⁵⁻¹³⁸ Three possible structures are conventionally found in the dimers: a liner molecule, an H-shaped dimer in which the mesogenic units are laterally attached and a T-shaped dimer containing a terminal and a laterally linked mesogenic unit. Examples are shown below:



Linear dimer



H-shaped dimer in which the mesogenic units are laterally attached

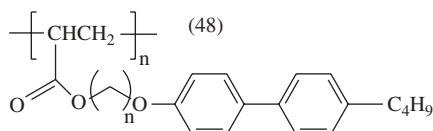
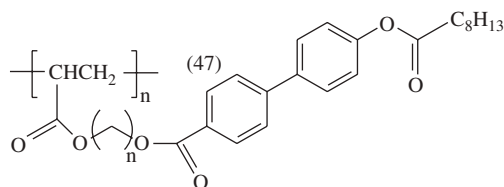
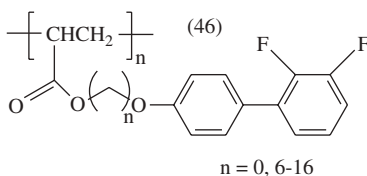


T-shaped dimer containing a terminal and a laterally linked mesogenic unit.

The linear dimer exhibits the highest clearing temperature and the lateral dimer the lowest. Smectic behaviour is observed only for the lateral dimers while the linear and T-shaped dimers exhibit solely nematic behaviour. This study considered only even spacers ($n = 4, 8$ and 12) and for all three series the clearing temperature decreases with increasing spacer length. It has been suggested that the strong nematic tendencies of the T-shaped dimers imply that the spacer adopts conformations for which the two mesogenic units are held more or less co-parallel. A wide variety of different systems have been studied and these support the general contention that whilst the rules for simple liquid crystals apply it is important to understand in detail the subtle influences which ultimately control the conformation of the chain and hence the ability to pack into either a crystalline or a mildly disordered form which is consistent with liquid crystalline behaviour.

3.12.6 Polymer Network Stabilized Liquid Crystal Phase

Polymer network stabilized ferroelectric liquid crystals with homogeneous alignment have been produced in cells without a surface alignment layer.^{139–141} Normally an alignment layer is required to achieve the desired orientation of the molecules for them to exhibit ferroelectric properties. In this approach, a crosslinkable monomer is mixed with the liquid crystal and polymerized in a magnetic field to form a polymer network that will stabilize the alignment of the ferroelectric liquid crystal.¹⁴² A concentration of the monomer of less than 10 wt% is required to avoid disturbance of the morphology of the low molecular weight material. The type of monomers which have been studied are shown below:



3.13 Structure Visualization

It will be appreciated that visualization of the structure of liquid crystalline materials is a particularly difficult task as the phase being studied has liquid-like character.¹⁴³ The technique of freeze fracture transmission electron microscopy allows examination of most systems; however, lyotropic materials which contain greater than 85% water still prove to be difficult. The technique involves the fast freezing of the material and then examination of the fracture surface. Despite the obvious attraction of this method it appears to be still in its infancy. Studies of cholesteric,¹⁴⁴ smectic¹⁴⁵ phases have been reported and show that it is possible to identify stacks of well-ordered materials which are often banana-shaped but do conform to the concepts that have been developed above.

3.14 Conclusions

Liquid crystals both as small molecule and polymeric materials will remain as fascinating materials and their useful physical properties will be used in many applications. We have not in this chapter considered two very important classes of liquid crystalline materials: lyotropic and naturally occurring materials. Lyotropic liquid crystals are formed when the concentration of the material is raised from dilute solution. They will often retain solvent as part of the phase structure and a wide range of phases can be observed depending on the concentration. They are discussed more fully in Chapter 11. Many celluloses, peptides, polysaccharides, *etc.*, have rigid backbone structures and hence can and do exhibit liquid crystalline behaviour. An example of one such system is hydroxypropylcellulose (HPC) that is a modified cellulose structure.¹⁴⁶ It is a semi-flexible polymer that can easily be aligned and exhibits the banded structure that is characteristic of the liquid crystalline state. Morphological features in naturally occurring systems are considered further in Chapter 11.

Recommended Reading

W.H. De Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon and Breach, London, 1980.

P.G. DeGennes, *The Physics of Liquid Crystals*, Oxford Science Publications, 1974.

G.R. Luckhurst and G.W. Gray, *The Molecular Physics of Liquid Crystals*, Academic Press, London, 1979.

I.W. Stewart, *The Static and Dynamic Continuum Theory of Liquid Crystals*, Taylor and Francis, London, 2004.

References

1. F. Reinitzer, *Monatsch Chem.*, 1888, **9**, 421–441 (English translation *Liq. Cryst.*, 1989, **5**, 7–18).

2. G. Friedel, *Ann. Phys. (Paris)*, 1922, **18**, 273–474.
3. H. Sackmann, *Liq. Cryst.*, 1989, **5**, 43–55.
4. P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, Clarendon Press, Oxford, 1993.
5. D. Demus, G. Kunicke, J. Neelson and H. Sackmann, *Z. Naturforsch.*, 1968, **23a**, 84; S. Diele, P. Brand and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, 1972, **17**, 1963.
6. A. De Vries and D.L. Fishel, *Mol. Cryst. Liq. Cryst.*, 1972, **16**, 311.
7. J. Doucet, A.M. Levelet and M. Lambert, *Phys. Rev. Lett.*, 1974, **32**, 301.
8. G.W. Gray and P.A. Windsor, in *Liquid Crystals and Plastic Crystals*, ed. G.W. Gray and P.A. Windsor, Ellis Horwood, Chichester, UK, 1974, vol. 1.
9. K. Markau and W. Maier, *Chem. Ber.*, 1962, **95**, 889.
10. W.H. de Jeu, *J Phys. (Paris)*, 1977, **38**, 1265.
11. G.W. Gray, *J. Phys. (Paris)*, 1975, **36**, 337; G.W. Gray, K.J. Harrison and J.A. Nash, *Electron Lett.*, 1973, **9**, 130.
12. J.W. Goodby and G.W. Gray, *J Phys. (Paris)*, 1976, **37**, 18.
13. G.W. Gray and D.G. McDonnell, *Mol. Cryst. Liq. Cryst.*, 1976, **37**, 189.
14. G.W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, New York, 1962, p. 131.
15. D. Coates and G.W. Gray, *J. Chem. Soc., Chem. Commun.* 1975, 514.
16. D. Coates and G.W. Gray, *Mol. Cryst. Liq. Cryst.*, 1976, **37**, 249.
17. D. Coates and G.W. Gray, *J. Chem. Soc., Perkin Trans. 2*, 1976, **7**, 863.
18. G.W. Gray, K.J. Harrison and J.A. Nash, *J. Chem. Soc., Chem. Commun.*, 1974, 431.
19. H.B. Burgi and J.D. Dunitz, *Helv. Chim. Acta*, 1970, **53**, 1747; J. van der Veen and A.H. Grobber, *Mol. Cryst. Liq. Cryst.*, 1971, **15**, 239.
20. G.W. Gray, in *The Molecular Physics of Liquid Crystals*, ed. G.R. Luckhurst and G.W. Gray, Academic Press, 1979, ch. 1.
21. J.M. Robertson and I. Woodward, *Proc. R. Soc. London, Ser. A*, 1937, **162**, 568.
22. M.J.S. Dewar and R.S. Goldberg, *J. Org. Chem.*, 1970, **35**, 2711; *J. Am. Chem. Soc.*, 1970, **92**, 1582.
23. M.J.S. Dewar, A.C. Griffin and R.M. Riddle, in *Liquid Crystals and Ordered Fluids*, ed. J.F. Johnson and R.S. Porter, Plenum Press, New York, 1973, vol. 2, p. 733; M.J.S. Dewar and R.M. Riddle, *J. Am. Chem. Soc.*, 1975, **97**, 6658; M.J.S. Dewar and A.C. Griffin, *J. Am. Chem. Soc.*, 1975, **97**, 662.
24. H.J. Deutscher, F. Kuschel, H. Schubert and D. Demus, *Deutsche Demokratische Republik Pat.*, DOS 24 29 093, 1975.
25. R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, *Angew. Chem.*, 1977, **89**, 103.
26. C. Weygand and R. Gabler, *Z. Phys. Chem.*, 1940, **B46**, 270.
27. H. Schubert, R. Dehne and V. Uhlig, *Z. Chem.*, 1972, **12**, 219.
28. W.R. Young, I. Haller and D.C. Green, *IBM Res. Rep.*, 1972, RC3827; *J. Org. Chem.*, 1972, **37**, 3707; W.R. Young and D.C. Green, *IBM Res. Rep.*, 1972, RC4121; *Mol. Cryst. Liq. Cryst.*, 1974, **26**, 7.

29. A.C. Griffin, D.L. Wertz and A.C. Griffin Jr, *Mol. Cryst. Liq. Cryst.*, 1978, **44**, 267.
30. W.H. de Jeu, *J. Phys. (Paris)*, 1977, **38**, 1265.
31. J. van der Veen, W.H. de Jeu, A.H. Grobбен and J. Boven, *Mol. Cryst. Liq. Cryst.*, 1972, **17** 291; W.H. de Jeu and J. van der Veen, *Philips Res. Rep.*, 1972, **27**, 172; J. van der Veen, W.H. de Jeu, M.W.M. Wanninkhof and C.A.M. Tienhoven, *J. Phys. Chem.*, 1973, **77**, 2153; W.H. de Jeu and Th.W. Lathouwers, *Z. Naturforsch.*, 1974, **A29**, 905.
32. G.W. Gray and P.A. Winsor, in *Liquid Crystals and Plastic Crystals*, ed. G.W. Gray and P.A. Winsor, Ellis Horwood, Chichester, UK, 1974, vol. 1.
33. G.W. Gray, in *Advances in Liquid Crystals*, ed. G.H. Brown, Academic Press, New York, 1976, vol. 2, p. 1.
34. G.W. Gray, *Mol. Cryst. Liq. Cryst.*, 1969, **7**, 127.
35. M. Leclerq, J. Billard and J. Jacques, *Mol. Cryst. Liq. Cryst.*, 1969, **8**, 367.
36. J.W. Goodby, G.W. Gray and D.G. McDonnell, *Mol. Cryst. Liq. Cryst.*, 1976, **34**, 183.
37. G.W. Gray, in *The Molecular Physics of Liquid Crystals*, ed. G.R. Luckhurst and G.W. Gray, Academic Press, 1979, ch. 12.
38. J.E. Lydon and C.J. Coakley, *J. Phys. (Paris)*, 1975, **36**, 45.
39. G.W. Gray and J.E. Lydon, *Nature (London)*, 1974, **252**, 221.
40. A.J. Leadbetter, J.L.A. Durrant and M. Rugman, *Mol. Cryst. Liq. Cryst. Lett.*, 1977, **34**, 231.
41. G.W. Gray and K.J. Harrison, *Symp. Faraday Soc.*, 1971, **5**, 54.
42. D.J. Byron, G.W. Gray, B.M. Worrall. *J. Chem. Soc.*, 1965, 3706.
43. M.A. Cotter, *Phys. Rev. A*, 1974, **10**, 625.
44. M.A. Cotter, *J. Chem. Phys.*, 1977, **66**, 1098.
45. M.A. Cotter, in *The Molecular Physics of Liquid Crystals*, ed. G.R. Luckhurst and G.W. Gray, Academic Press, 1979, ch. 12.
46. C. Zannoni, in *The Molecular Physics of Liquid Crystals*, ed. G.R. Luckhurst and G.W. Gray, Academic Press, 1979, ch. 3.
47. G.R. Luckhurst, in *The Molecular Physics of Liquid Crystals*, ed. G.R. Luckhurst and G.W. Gray, Academic Press, 1979, ch. 4.
48. W. Maier and A. Saupe, *Z. Naturforsch. A*, 1958, **13**, 564.
49. W. Maier and A. Saupe, *Z. Naturforsch. A*, 1959, **14**, 882.
50. F.M. Leslie, *Quart. J. Mech. Appl. Math.*, 1966, **19**, 357.
51. F.M. Leslie, *Arch. Rat. Mech. Anal.*, 1986, **28**, 265.
52. C. Zannoni, in *The Molecular Physics of Liquid Crystals*, ed. G.R. Luckhurst and G.W. Gray, Academic Press, 1979, ch. 9.
53. N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, *J. Chem. Phys.*, 1953, **21**, 1087.
54. M.A. Bates, *Liq. Cryst.*, 2005, **32**(11), 1365–1377.
55. J.G. Gay and B.J. Berne, *J. Chem. Phys.*, 1981, **74**, 3316.
56. J. Corner, *Proc.R. Soc. London, Ser. A*, 1948, **192**, 275.
57. M.A. Bates and G.R. Luckhurst, *Struct. Bond.*, 1999, **94**, 65.
58. S. Chandrasekar, in *Polymers Liquid Crystals and Low Dimensional Solids*, ed. N. March and M. Tosi, Plenum Press, New York, 1984, ch. 7.

59. G. Durand, in *Polymers, Liquid Crystals and Low Dimensional Solids*, ed. N. March and M. Tosi, Plenum Press, New York, 1984, ch. 11.
60. I.W. Stewart, *The Static and Dynamic Continuum Theory of Liquid Crystals*, Taylor & Francis, London, 2004.
61. B.S. Scheuble, *Kontakte (Darmstadt)*, 1989, **1**, 34–48.
62. F. Schneider and H. Knepe, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Gooby, G.W. Gray, H.W. Spiess and V. Vill, Wiley VCH, Weinheim, 1998, vol. 1, pp. 454–476.
63. V. Sergan and G. Durand, *Liq. Cryst.*, 1995, **18**, 171–174.
64. M.J. Stephen and J.P. Straley, *Rev. Mod. Phys.*, 1974, **46**, 617–704.
65. L. Onsager, *Ann. N.Y. Acad. Sci.*, 1949, **51**, 627.
66. P.J. Flory, *Proc. R. Soc. London, Ser. A*, 1956, **234**, 73.
67. A. Roviello and A. Sirigu, *J. Polym. Sci., Polym. Lett. Ed.*, 1975, **13**, 455.
68. M. Gordon and N.A. Plate (eds), *Adv. Polym. Sci.*, 1984, 60/61.
69. A. Blumstein, *Mesomorphic Order in Polymers and Polymerization in Liquid Crystalline Media*, ACS Symposium Series 74, American Chemical Society, Washington, DC, 1978.
70. A. Blumstein, *Liquid Crystalline Order in Polymers*, Academic Press, New York, 1978.
71. A. Blumstein, *Polymeric Liquid Crystals*, Plenum Press, New York, 1985.
72. L.L. Chapoy, *Recent Advances in Liquid Crystalline Polymers*, Elsevier, London, 1985.
73. A. Ciferri, W.R. Krigbaum and R.B. Meyers, *Polymer Liquid Crystals*, Academic Press, London, 1982.
74. C.B. McArdle, *Side Chain Liquid Crystal Polymers*, Blackie, Glasgow, 1989.
75. A. Ciferri (ed.), *Liquid Crystallinity in Polymers. Principles and Fundamental Properties*, VCH, New York, 1991.
76. R.A. Weiss and C.K. Ober, *Liquid Crystalline Polymers*, ACS Symposium Series 435, American Chemical Society, Washington, DC, 1990.
77. E. Chiellini and R.W. Lenz, in *Comprehensive Polymer Science*, ed. G. Allen and J.C. Bevington, Pergamon Press, Oxford, 1989, vol. 5, p. 701.
78. R. Zentel, in *Comprehensive Polymer Science*, ed. G. Allen and J.C. Bevington, Pergamon Press, Oxford, 1989, vol. 5, p. 723.
79. A.M. Donald and A.H. Windle, *Liquid Crystalline Polymers*, Cambridge University Press, Cambridge, 1991; C. Noel and P. Navard, *Prog. Polym. Sci.*, 1991, **16**, 55.
80. V. Percec and D. Tomazos, in *Comprehensive Polymer Science*, ed. S. Aggawal, S. Russo and G. Allan, Pergamon Press, 1992, 1st supplement, ch. 14, p300.
81. J. Moon, J.H. Ford and S. Yang, *Polym. Adv. Technol.*, 2006, **17**(2), 83–93.
82. J. Moon, J.H. Ford and S.J. Yang, *Macromol. Sci. Polym. Rev.*, 2005, **C45**(4), 351–373.
83. J. Qi and G.P. Crawford, *Displays*, 2004, **25**(5), 177–186.
84. J. Gu, Y. Xu, Y.S. Liu, J.J. Pan, F.Q. Zhou and H. He, *J. Opt. A: Pure Appl. Opt.*, 2003, **5**(6), S420–S427.

85. J.M. Mucha, *Prog. Polym. Sci.*, 2003, **28**(5), 837–873.
86. T.J. Bunning, L.V. Natarajan, V.P. Tondiglia and R.L. Sutherland, *Annu. Rev. Mater. Sci.*, 2000, **30**, 83–115.
87. L. Bouteiller and P. Lebarney, *Liq. Cryst.*, 1996, **21**(2), 157–174.
88. A. Blumstein, S. Vilasagar, S. Ponrathnam, S.B. Clough, R.B. Blumstein and G. Maret, *J. Polym. Sci., Polym. Phys., Ed.*, 1982, **20**, 877.
89. V. Percec, H. Nava and H. Jonsson, *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25**, 1943.
90. J.L. Feijoo, G. Ungar, A.J. Owen, A. Keller and V. Percec, *Mol. Cryst. Liq. Cryst.*, 1988, **155**, 487.
91. V. Percec and D. Tomazos, *Polymer*, 1990, **31**, 1658; V. Percec, B. Hahn, M. Ebert and J.H. Wendorff, *Macromolecules*, 1990, **23**, 2092.
92. S.G. Kostromin, R.V. Talrose, V.P. Shibaev and N.A. Plate, *Makromol. Chem. Rapid Commun.*, 1982, **3**, 803.
93. Y.K. Godovsky, I.I. Mamaeva, N.N. Makarova, V.P. Papkov and N.N. Kuzmin, *Makromol. Chem. Rapid Commun.*, 1985, **6**, 797.
94. V. Percec and B. Hahn, *Macromolecules*, 1989, **22**, 1588.
95. V. Percec, M. Lee and H. Jonsson, *J. Polym. Sci., Polym. Chem. Ed.*, 1991, **29**, 327.
96. V. Percec and M. Lee, *J. Macromol. Sci. Chem.*, 1991, **A28**, 651.
97. V. Percec, M. Lee and C. Ackerman, *Polymer*, 1992, **33**, 703.
98. V. Percec and M. Lee, *Macromolecules*, 1991, **24**, 2780.
99. V. Percec, A.D.S. Gomes and M. Lee, *J. Polym. Sci., Polym. Chem. Ed.*, 1991, **29**, 1615.
100. V. Percec, C.S. Wang and M. Lee, *Polym. Bull.*, 1991, **26**, 15.
101. V. Percec, Q. Zheng and M. Lee, *J. Mater. Chem.*, 1991, **1**, 611.
102. J. Majnusz, J.M. Catala and R.W. Lenz, *Eur. Polym. J.*, 1983, **19**, 1043.
103. Q.F. Zhou, X.Q. Duan and Y.L. Liu, *Macromolecules*, 1986, **19**, 247.
104. V. Percec and H. Nava, *J. Polym. Sci., Polym. Chem. Ed.*, 1987, **25**, 405.
105. H. Stevens, G. Rehage and H. Finkelmann, *Macromolecules*, 1984, **17**, 851.
106. P.J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, 1979, **54**, 311.
107. P.A. Irvine, W. Dacheng and P.J. Flory, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 1795.
108. V. Percec, D. Tomazos and C. Pugh, *Macromolecules*, 1989, **22**, 3259.
109. W. Kern, W. Gruber and H.O. Wirth, *Makromol. Chem.*, 1960, **37**, 198.
110. J.K. Stille, F.W. Harris, R.O. Rakutis and H. Mukamal, *J. Polym. Sci., Polym. Lett. Ed.*, 1966, **4**, 791.
111. H. Mukamal, F.W. Harris and J.K. Stille, *J. Polym. Sci., Part A-1*, 1967, **5**, 2721.
112. J.K. Stille, R.O. Rakutis, H. Mukamal and F.W. Harris, *Macromolecules*, 1968, **1**, 431.
113. (a) W. Heitz and H.W. Schmidt, *Makromol. Chem., Macromol. Symp.*, 1990, **38**, 149; (b) H. Kromer, R. Kuhn, H. Pielartzik, W. Siebke, V. Eckhardt and M. Schmidt, *Macromolecules*, 1991, **24**, 1950; (c) B.S. Hsiao, R.S. Stein, N. Weeks and R. Gaudiana, *Macromolecules*, 1991, **24**, 1299.

114. M. Wenzel, M. Ballauff and G. Wegner, *Makromol. Chem.*, 1987, **188**, 2865.
115. F.H. Metzmann, M. Ballauff, R.C. Schulz and G. Wegner, *Makromol. Chem.*, 1989, **190**, 985.
116. R. Duran, M. Ballauff, M. Wenzel and G. Wegner, *Macromolecules*, 1988, **21**, 2897.
117. F.W. Harris and S.L.C. Hsu, *High Perform. Polym.*, 1989, **1**, 3.
118. H.R. Kricheldorf and J. Awe, *Makromol. Chem., Rapid Commun.*, 1988, **9**, 681.
119. H.R. Kricheldorf and J. Jenssen, *Eur. Polym. J.*, 1989, **25**, 1973.
120. H.R. Kricheldorf and J. Awe, *Makromol. Chem.*, 1989, **190**, 2579.
121. P.J. Stenhouse, E.M. Valles, S.W. Kantor and W.J. MacKnight, *Macromolecules*, 1989, **22**, 1467.
122. H.R. Kricheldorf and D. Lubbers, *Makromol. Chem., Rapid Commun.*, 1990, **11**, 303.
123. H.R. Kricheldorf and R. Pakull, *Macromolecules*, 1988, **21**, 551.
124. H.R. Kricheldorf and R. Pakull, *Polymer*, 1987, **28**, 1772.
125. H.R. Kricheldorf, R. Pakull and S. Buchner, *Macromolecules*, 1988, **21**, 1929.
126. L. Noirez, J.P. Cotton, F. Hardouin, P. Keller, F. Moussa, G. Pepy and C. Strazielle, *Macromolecules*, 1988, **21**, 2889.
127. P. Davidson, L. Noirez, J.P. Cotton and P. Keller, *Liq. Cryst.*, 1991, **10**, 111.
128. F. Hardouin, S. Mery, M.F. Achard, L. Noirez and P. Keller, *J. Phys.*, 1991, **1**, 511.
129. H. Mattoussi, R. Ober, M. Veysie and H. Finkelmann, *Europhys. Lett.*, 1986, **2**, 233.
130. F. Kuschel, A. Madicke, S. Diele, H. Utschik, B. Hisgen and H. Ringsdorf, *Polym. Bull.*, 1990, **23**, 373.
131. P.W. Morgan, *Macromolecules*, 1977, **10**, 1381; S.L. Kwolek, P.W. Morgan, J.R. Shaefgen and L.W. Gulrich, *Macromolecules*, 1977, **10**, 1390; T.I. Bair, P.W. Morgan and F.L. Killian, *Macromolecules*, 1977, **10**, 1396; M. Panar and L. Beste, *Macromolecules*, 1977, **10**, 1401.
132. R.D. Richards, W.D. Hawthorne, J.S. Hill, M.S. White, D. Lacey, J.A. Semiyen, G.W. Gray and T.C. Kendrick, *J. Chem. Soc., Chem. Commun.*, 1990, **95**.
133. V. Percec and C. Pugh, in *Side Chain Liquid Crystal Polymers*, ed. C.B. McArdle, Chapman and Hall, New York, 1989, p. 30.
134. G.W. Gray, in *Side Chain Liquid Crystal Polymers*, ed. C.B. McArdle, Blackie, Glasgow, 1989, p. 106.
135. C.B. McArdle (ed.), *Side Chain Liquid Crystalline Polymers*, Blackie, Glasgow, 1989.
136. C.T. Imrie and P.A. Henderson, *Curr. Opin. Colloid Interf. Sci.*, 2002, **7**, 298–311.
137. C.T. Imrie and G.R. Luckhurst, in *Handbook of Liquid Crystals*, ed. D. Demus, J.W. Goodby, G.W. Gray and H.W. Spiess, Wiley VCH, Weinheim, 1998, vol. 2B, pp. 801–833.

138. C.T. Imrie, *Struct. Bond.*, 1999, **95**, 149–192.
139. W.-S. Bae, J.-W. Lee and J.-I. Jin, *Liq. Cryst.*, 2001, **28**, 59–67.
140. W. Zheng and G.H. Milburn, *Liq. Cryst.*, 2000, **27**, 1423–1430.
141. R.A.M. Hikmet, H.M.J. Boots and M. Michielsen, *Liq. Cryst.*, 1995, **19**, 65–76.
142. A.C. Guymon, E.N. Hoggan, D.M. Walba, C.N. Clark and C.N. Bownam, *Liq. Cryst.*, 1995, **19**, 719–727.
143. O. Mondain-Monval, *Curr. Opin. Colloid Interf. Sci.*, 2005, **10**, 250–255.
144. D.W. Berrman, S. Meiboom, J.A. Zasadzinski and M.J. Sammon, *Phys. Rev. Lett.*, 1986, **57**, 1737–1740.
145. J. Fernsler, L. Hough, R.F. Shao, J.E. Maclennan, L. Navailles, O. Madhusudham, O. Mondain-Monval, C. Boyer, J. Zasadzinski, J. Rego, D.M. Walba and N.A. Clark, *Proc. Natl Acad. Sci. USA*, 2005, **4**, 14191–14196.
146. C. Viney and W.S. Putnam, *Polymer*, 1995, **36**, 1731.

CHAPTER 4

Plastic Crystals

4.1 Introduction

In the previous chapters the properties of ordered and disordered low molecular weight organic materials have been considered, so as to help to develop our understanding of the factors which will influence the organization in high molar mass materials. Smectic liquid crystalline materials exhibit a higher degree of order, yet still retain at least one degree of freedom. Plastic and incommensurate phase materials similarly exhibit a high degree of order, yet, over a limited temperature range, retain a degree of freedom. As we shall see when we consider polymers, the ability to exhibit some level of motional freedom, yet still have solid characteristics is a very important and useful characteristic of polymers.

4.2 Plastic Crystalline Materials

In Chapter 2, the structural characteristics of a range of organic crystals were considered. Using appropriate conditions it is possible to grow large single crystals of materials such as carbon tetrabromide,¹ adamantane,² bicyclooctane,² camphene,² norbornylene,² succinonitrile,² pivalic acid,² hexamethylethane,² *etc.* An example of such a crystal is shown in Figure 4.1.

Superficially these materials show sharp melting transitions that would indicate that they are behaving as simple crystals. However, if one studies carefully a number of their physical properties it becomes evident that there is a transition that allows a degree of molecular motion to be achieved in these systems below the melting temperature. Examination of the molecular structure of these molecules indicates that they all have a common feature, a spherical shape (Figure 4.2). The lattice structure of carbon tetrabromide is a face-centred cubic material. Examination of the melting process using differential scanning calorimetry (DSC) indicates that instead of the single melt peak expected, there is a second lower temperature peak occurring at 320.9 °C, which is significantly below the melting point at 366.4 °C (Figure 4.3). The DSC trace clearly shows the two shape peaks. The ultrasonic velocity decreases in an

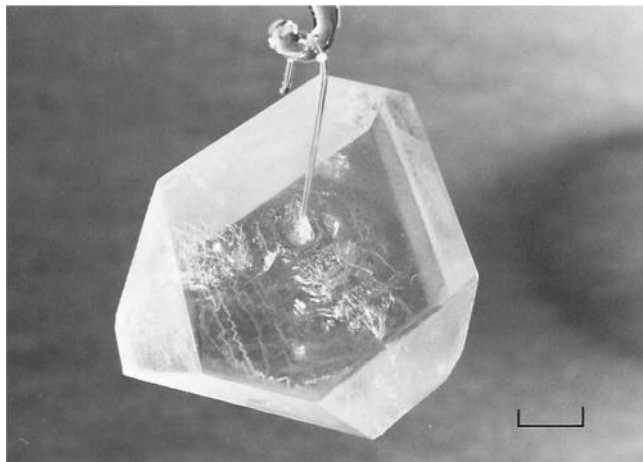


Figure 4.1 Single crystal of carbon tetrabromide grown from ethanol solution (scale bar = 1 cm).¹

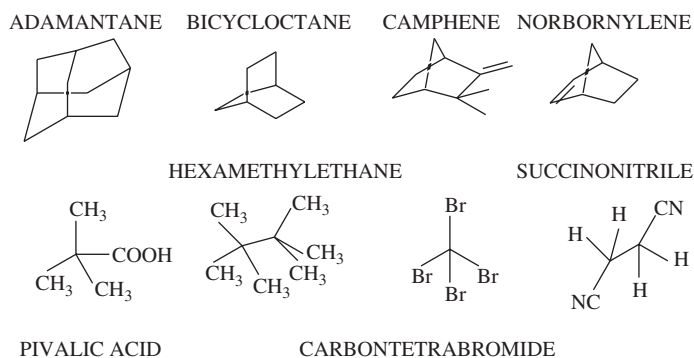


Figure 4.2 Structures of some plastic crystalline materials.

approximately linear manner as the temperature is increased, consistent with the expected decrease in the elastic modulus. At 320.9 °C, the velocity drops to a value below 1100 m s⁻¹ and it becomes difficult to measure the value because the sound waves have become highly attenuated. This behaviour is unexpected as the material is still a solid.

This sudden drop in the velocity is associated with the carbon tetrabromide molecule suddenly gaining the freedom to rotate on its axis without the ability to undergo translation. The onset of translation is marked by the melting transition at 366.4 °C. The tetrahedral molecule below 320.9 °C is locked into the crystal structure and the C–Br bonds point in well-defined directions. At 320.9 °C the lattice expansion allows the molecule to rotate on its lattice point and being a pseudo-spherical molecule, the average force field has an

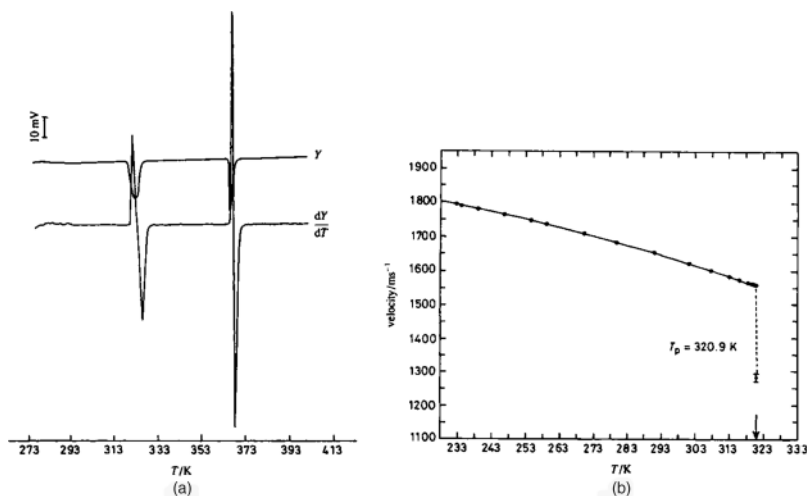


Figure 4.3 Differential scanning calorimetry trace (a) and ultrasonic velocity scan (b) as a function of temperature for carbon tetrabromide.

approximately spherical form. Studies of so-called ‘globular molecules’³ indicated that for molecules with the formula (CXYZW), where the groups involved are CH₃, NO₂, and Cl for X, Y and Z and W may be CN or Br, then rotor–plastic phase behaviour is observed. Another sequence identified was based on the simple polar derivatives of camphene and cyclohexane derivatives. Measurements of the dielectric permittivity as a function of temperature exhibited unusual behaviour⁴ (Figure 4.4).

It would be expected that when a polar liquid is frozen, the dipoles would become immobilized and the permittivity would decrease. In the case of 2-chloro-2-nitropropane the reverse appears to occur with the magnitude of the permittivity increasing on freezing. Similar behaviour has been observed for all the rotator phase materials, the magnitude of the effect varying from system to system.^{4–9} Normally the amplitude of the dipole relaxation will be governed by the distribution of states that it can occupy. In the liquid state the dipole is restricted by the shape of the potential formed by the neighbouring molecules (Figure 4.5). In the rotator phase, the potential has now become symmetric and more effective rotation of the dipole is possible.

In these simple molecules, the dielectric relaxation curves conform to the simple Debye form and hence it is relatively straightforward to determine activation energies from the variation of the relaxation frequency with temperature (Table 4.1). A surprising feature of the rotator phase is that in certain cases the activation for dipolar relaxation is smaller in the solid than it is in the liquid phase, when the solid conforms to a face-centred cubic lattice. When the solid melts, the local force field loses its symmetrical form and the result is that the activation energy for free rotation is observed to increase slightly (Figure 4.5). For most polar liquids, the activation energy for viscosity flow and for dipole

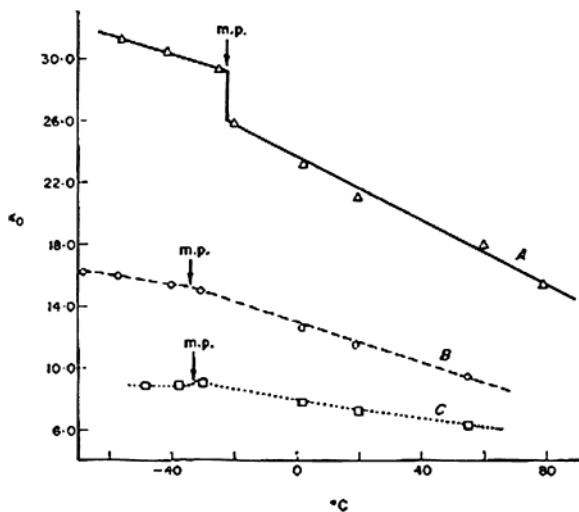


Figure 4.4 Permittivity values (ϵ_0) for 'spherical' methane derivatives in the liquid and solid phases. A: 2-chloro-2-nitropropane, $\text{CH}_3\text{CCINO}_2\text{CH}_3$; B: 2,2-dichloropropane, $\text{CH}_3\text{CCl}_2\text{CH}_3$; C: 1,1,1-trichloroethane, CCl_3CH_3 .⁴

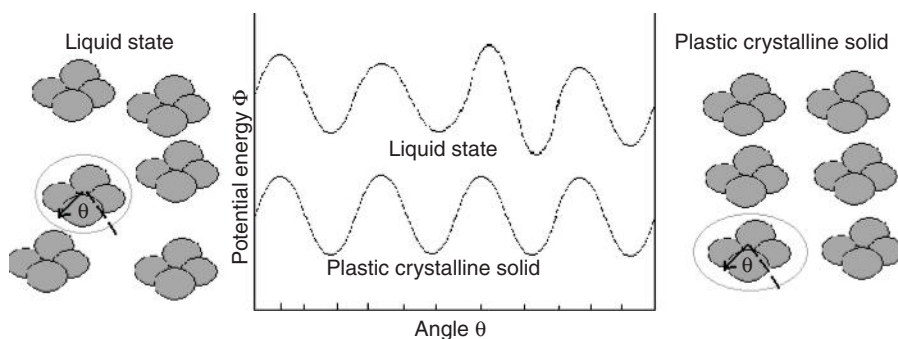


Figure 4.5 Variation of the potential energy with rotation angle: (a) the liquid state; (b) the plastic crystalline state.

relaxation are very similar, but in the case of the pseudo-spherical substituted methanes the activation energy of the rotational process is approximately half that for viscous flow. The reason for this difference is that translational motion of the neighbouring molecules in the fluid is coupled and higher energy is observed for motion. In the solid phase, the translational motion ceases and the activation energy is that for the dipole rotation in a pseudo-spherical force field.

Another group of dielectrically interesting solids are the polysubstituted aromatics having at least four halogen, nitro or methyl group substituents. These molecules have the symmetry of circular discs and exhibit ready rotation about one axis.¹⁰ Two examples of such systems are presented in Table 4.1.

Table 4.1 Activation enthalpies for molecular rotation in liquids and solids.

Molecule	ΔH^*_E (kJ mol ⁻¹), solid	ΔH^*_E (kJ mol ⁻¹), liquid	ΔH^*_E (kJ mol ⁻¹), viscosity	Ref
(CH ₃) ₂ CCl ₂	5.8	5.2	10.5	4
CCl ₃ CH ₃	4.6	4.7	10.7	4
(CH ₃)CNO ₂	2.1	3.4	14.0	4
(CH ₃)CCINO ₂	5.5	6.1	13.6	4
Succinonitrile	8.8	13.0	–	8
Camphene	9.2	–	–	4
Camphor	7.5	–	–	4
Bornyl chloride	10.4	–	–	4
Isoborneol	23.0	–	–	4
Pentachlorotoluene	49.7	–	–	9
1,2,4-Trimethyl-3,5,6-trichlorobenzene	44.3	–	–	9

A variety of other systems have been studied and include organic ions such as the butylammonium salts,^{11,12} substituted cyclohexanes,¹³ cyanoadamantane,¹⁴ chloroadamantane,¹⁴ tetrachloro-*m*-xylene,¹⁵ pentachloronitrobenzene,¹⁶ caffeine¹⁷ and various zinc chloride salts ((*n*-C₅H₁₁NH₃)₂ZnCl₄ and (*n*-C₁₂H₂₅NH₃)₂ZnCl₄).¹⁸ All these systems support the concept that in the rotator–plastic phase motion is easier than in the liquid and that it only ceases when the strength of the intermolecular interactions is sufficiently strong to impose an asymmetric profile on the pseudo-spherical cavity.

4.3 Alkanes and Related Systems

Although the initial studies of the rotator phase were concerned with molecules which have a pseudo-spherical shape, it was found that other molecular systems were able to exhibit rotational motion in the solid state. Liquid crystals possess mesophase characteristics because of the rotational freedom about one of their axes. The alkanes have received considerable attention over the years and are precursors for the study of polymers. Methane and propane are pseudo-spherical and will in principle have rotator phases but these occur at very low temperature and are difficult to access. In Chapter 1, the possibility of *gauche*–*trans* isomerism was discussed in the context of *n*-alkane chains. Analysis of the dynamic distribution of molecular shapes at the melting point temperature has been carried out in order to estimate the length of the alkane chain exhibiting the first premelting transition.^{19,20} This study indicates that nonane (*n* = 9) is the first linear hydrocarbon to exhibit a premelt transition. However, the majority of studies have been carried out with longer chain lengths.

X-Ray scattering studies of octadecane, CH₃(CH₂)₁₆CH₃, and other even chain length alkanes in their triclinic phase formed by the supercooling of melt, have shown that a transient metastable rotator phase exists. Such metastable and transient phases are likely to have analogues in polymeric systems.^{21–23}

Molecular dynamics simulations have been used to provide a better understanding of the processes occurring on cooling *n*-nonadecane.²⁴ A molecular dynamics simulation of the free surface of the melt have been carried out using three layers of lamellas and studied over the a temperature range (385–410 K). In this range the middle layer prefers to be in the melt state with both surface layers remaining crystalline and reflects the experimental observation of surface freezing found in *n*-alkanes. It is found that the molecules in the surface monolayer align their axes nearly perpendicular to the surface and form well-defined hexagonal packing. It is also found that the molecules in the surface monolayer show large centre-of-mass fluctuations, translational and transverse, along the surface normal and parallel to the surface, respectively. The chains in the middle are therefore exhibiting characteristics of a rotator phase.

Investigations of mixtures of alkanes for $C_{19}H_{40}$ – $C_{20}H_{42}$ indicate that the temperature range of the rotator phase widens due to chain mixing.²⁵ Eicosane has also been studied and X-ray scattering measurements indicate the existence of a rotator phase.²⁶ Studies of the ultrasonic attenuation and DSC measurements²⁷ (Figure 4.6) and Raman scattering²⁸ have indicated that between 33.3 °C and 36.6 °C there exists a rotator phase as evidenced by a marked drop in the velocity from the expected linear behaviour. The DSC traces show a clear shoulder prior to the main melting peak which is indicative of the existence of the rotator phase.

Raman scattering studies²⁸ indicated the concentration of *gauche*–*trans* defects increased continuously with increasing temperature and these defects can be associated with the ends of the chain.

The diffusion coefficients in a number of *n*-alkanes have been investigated,^{29,30} which show the influence of the rotator phase assisting the motion of the polymer chains. Rotator phases have been reported in chains with as many as 36 carbon atoms.^{31,32} Measurements of DCS and X rays scattering^{33–36}

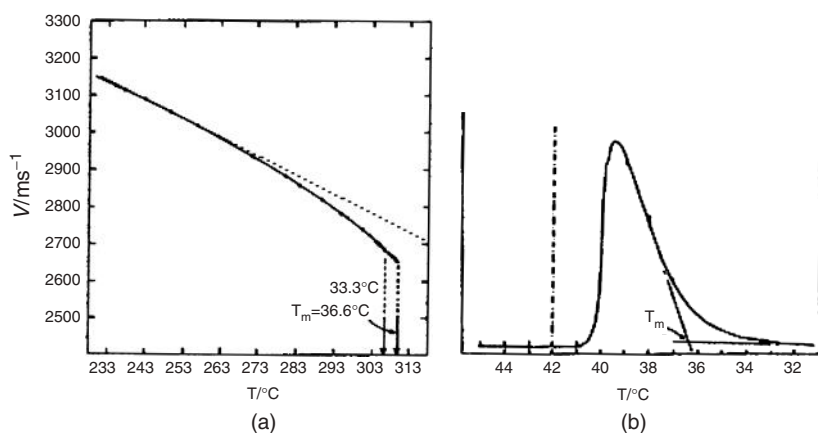


Figure 4.6 Plot of the acoustic velocity in the chain direction (a) and the DSC trace (b) for the melting of eicosane. The dotted line in (a) indicates the linear extrapolation of the velocity from low temperature.

of a number of *n*-alkane systems have confirmed the existence of the rotator phase.

4.4 Conclusions

Rotator phase materials are related to liquid and molecular crystals, discussed in Chapters 2 and 3. The rotator phase is characterized by the following:

- in low molecular mass materials the molecules exhibit almost free rotation yet are fixed on their lattice points, and
- in the short-chain alkanes the chains are free to rotate about their molecular axis and also exhibit enhanced diffusion coefficients due to their ability to move down the cylinders as a consequence of the free rotation of the chains.

This mobility close to the melt temperature is very important in understanding the behaviour of polymer materials in the crystalline state and is considered in subsequent chapters.

Recommended Reading

J.N. Sherwood (ed.), *Plastically Crystalline State*, Wiley, Chichester, UK, 1970.

References

1. C.S. Yoon, J.N. Sherwood and R.A. Pethrick, *J. Chem. Soc., Faraday Trans.*, 1989, **85**(9), 2867.
2. M. Eldrup, D. Lightbody and J.N. Sherwood, *Chemical Physics*, 1981, **63**(1-2), 51–58.
3. J. Timmermans, *Les Constantes Physiques des composés organiques cristallins*, Masson, Paris, 1953.
4. C. Clemett and M. Davis, *Trans. Faraday Soc.*, 1962, **58**, 1705.
5. J.G. Powles, *J. Chem. Phys.*, 1952, **20**, 1048.
6. A.H. White and W.S. Bishop, *J. Am. Chem. Soc.*, 1940, **62**, 16.
7. C.P. Smyth, *Trans. Faraday Soc.*, 1946, **42A**, 175.
8. C. Clemett and M. Davis, *J. Chem. Phys.*, 1960, **29**, 1347.
9. A. Turney, *Proc IEE*, 1953, **100**, 46.
10. A. Gerschel, I. Darmon and C. Brot, *Molecular Physics*, 1972, **23**(2), 317.
11. M. Hattori, S.I. Fukada, D. Nakamura and R. Ikeda, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3777–3783.
12. M. Hattori, Y. Onoda, T. Erata, M.E. Smith, M. Hattori, H. Ohki and R. Ikeda, *Z. Naturforsch. A*, 1994, **49**, 291–296.

13. T.M.R. Maria, F.S. Costa, M.L.P. Leitao and J.S. Redinha, *Thermochim. Acta*, 1995, **269**, 405–413.
14. J. F. Willart, M. Descamps and N. Benzakour, *J. Chem. Phys.*, 1996, **104**, 2508–2517.
15. J.J.M. Ramos, R.J.C. Sousa, N.T. Correia and M.S.C. Dionisio, *Ber. Bunsen-Ges. Phys. Chem.*, 1996, **100**(5), 571–577.
16. J.J. M. Ramos, N.T. Correia and M.J. Teixeira, *Mol. Cryst. Liq. Cryst. C*, 1996, **6**(3), 205–214.
17. M. Descamps, N.T. Correia, P. Derollez, F. Danede and F. Capet, *J. Phys. Chem. B*, 2005, **109**(33), 16092–16098.
18. K. Horiuchi, H. Takayama, S. Ishimaru and R. Ikeda, *Bull. Chem. Soc. Jpn.*, 2000, **73**(2), 307–314.
19. G.A. Arteca, *J. Phys. Chem. B*, 1997, **101**(20), 4097–4104.
20. B. Zgardzinska, J. Wawryszczuk and T. Goworek, *Chem. Phys.*, 2006, **320**(2–3), 207–213.
21. E.B. Sirota and A.B. Herhold, *ACS Symp. Ser.*, 2000, **739**, 232–241.
22. I.V. Filippova, E.N. Kotelnikova, S.Y. Chazhengina and S.K. Filatov, *J. Struct. Chem.*, 1998, **39**(3), 307–317.
23. I. Denicolo, J. Doucet and A.F. Craievich, *J. Chem. Phys.*, 1983, **78**(3), 1465–1469.
24. H.Z. Li and T. Yamamoto, *J. Chem. Phys.*, 2001, **114**(13), 5774–5780.
25. A.B. Herhold, H.E. King and E.B. Sirota, *J. Chem. Phys.*, 2002, **116**(20), 9036–9050.
26. B.M. Ocko, E.B. Sirota, M. Deutsch, E. DiMasi, C.S. Coburn, J. Strzalka, S.Y. Zheng, A. Tronin, T. Gog and C. Venkataraman, *Phys. Rev. E*, 2001, **63**, 33.
27. C.S. Yoon, J.N. Sherwood and R.A. Pethrick, *J. Chem. Soc., Faraday Trans. I*, 1989, **85**(10), 3221–3232.
28. M. Maroncelli, S.P. Qi, H.L. Strauss and R.G. Snyder, *J. Am. Chem. Soc.*, 1982, **104**, 6237.
29. T. Yamamoto, H. Aoki, S. Miyaji and K. Nozaki, *Polymer*, 1997, **38**(11), 2643–2647.
30. H. Yamakawa, S. Matsukawa, H. Kurosu, S. Kuroki and I. Ando, *J. Chem. Phys.*, 1999, **111**(15), 7110–7115.
31. H. Honda, S. Tasaki, A. Chiba and H. Ogura, *Phys. Rev. B*, 2002, **65**(10), 104112.
32. F. Mina, T. Asano, D. Mondieig, A. Wurflinger and C. Josefiak, *J. Phys. IV*, 2004, **113**, 35–38.
33. S.L. Wang, K. Tozaki, H. Hayashi, S. Hosaka and H. Inaba, *Thermochim. Acta*, 2003, **408**, 1–2.
34. K. Kato and T. Seto, *Jpn. J. Appl. Phys. Part 1*, 2002, **41**(4A), 2139–2145.
35. K. Nozaki, T. Yamamoto, T. Hara and M. Hikosaka, *Jpn. J. Appl. Phys. Part 2*, 1997, **36**(2A), L146–L149.
36. H. Honda, S. Tasaki, A. Chiba and H. Ogura, *Phys. Rev. B*, 2002, **65**(10), 104112.