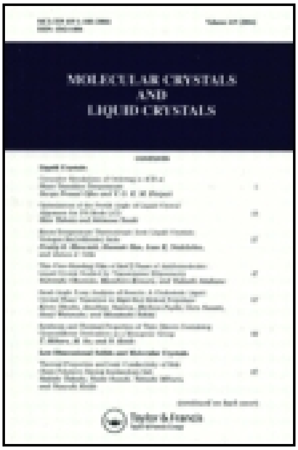


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Ferroelectric Liquid Crystals - Structure and Design

J. W. Goodby [a] & T. M. Leslie [b]
[a] AT&T Bell Laboratories Murray Hill, NJ, 07974, USA
[b] AT&T Bell Laboratories Murray Hill, NJ, 07974

To cite this article: J. W. Goodby & T. M. Leslie (1984): Ferroelectric Liquid Crystals - Structure and Design, Molecular Crystals and Liquid Crystals, 110:1-4, 175-203

To link to this article: http://dx.doi.org/10.1080/00268948408074505

Mol. Cryst. Liq. Cryst. 1984, Vol. 110, pp. 175-203
0026-8941/84/1104-0175/$18.50/0

Printed in the United States of America

FERROELECTRIC LIQUID CRYSTALS - STRUCTURE AND DESIGN

J. W. GOODBY
AT&T Bell Laboratories
Murray Hill, NJ 07974 USA

T. M. LESLIE
AT&T Bell Laboratories
Murray Hill, NJ 07974

Interest in the synthesis of optically active smectic liquid crystals has increased considerably since the advent of a fast switching, bistable, electrooptic device configuration based on their ferroelectric properties. A number of structurally separate ferroelectric liquid crystal phases have been defined which possess differing properties. These types of phase can be utilized in different forms of application. The structures of the various ferroelectric smectic phases and the types of material which exhibit these modifications are discussed in detail. The design and engineering of materials to suit certain device criteria is related to the properties of the smectic ferroelectric phases. A relationship between the absolute spacial configuration of the optically active materials which exhibit ferroelectric smectic phases, the twist direction of the phase and the direction of the spontaneous polarization is developed.

INTRODUCTION

The advent of a bistable, fast-switching, electrooptic light-valve based on the properties of ferroelectric smectic liquid crystals[1] has aroused considerable interest in the synthesis and engineering of new smectogens suitable for applications of this nature. As with the development of other liquid crystal electrooptic concepts, for example, the twisted nematic and guest-host systems, materials need to be designed to suit certain parameters required by the device configuration. At present, however, many investigations into the properties of ferroelectric phases are still being carried out on the phases of substances[2] that have been known for a long period of time, and which have been shown to be thermally unstable.[21]

In novel electrooptic concepts based on the properties of ferroelectric liquid crystals, the characteristics required of materials depend to a large extent on the phase that is to be employed. Although many studies have concentrated solely on the chiral smectic C* phase, there are at least six other different ferroelectric smectic phases that have not yet been fully explored,[3] and which may possibly be employed in different forms of application. However, the materials needed to produce these various ferroelectric modifications require different kinds of engineering. For example, in some applications of the C* phase,[1] materials are required which exhibit a high spontaneous polarization, have a wide temperature range, have a long helical pitch length, are stable, exhibit a smectic A phase on cooling from the isotropic liquid for alignment purposes, and have low viscosities. In addition to these specifications, the J* phase for instance, would also require an extremely high spontaneous polarization, and a very low viscosity. It may be argued therefore that the requirements placed on molecular design are, in fact, far more rigorous for applications of ferroelectric phases than those that were sought after in the early stages of the development of materials for the twisted nematic device.

In the following sections the structures and properties of each ferroelectric smectic phase and the guidelines for the development of ferroelectric smectogens suitable for applications are discussed.

1. Classification and Structure of the Ferroelectric Phases

Seven smectic phases (C, I, F, J, G, K, and H) have been defined which have structures where the long axes of their constituent molecules are tilted with respect to their layer planes. The individual molecules in each of these phases can be described as possessing a local ***monoclinic environment***. This structuring possesses the following symmetry elements; a two-fold axis of rotation parallel to the layer planes, a center of inversion, and a mirror plane normal to the tilt direction. If the phase is constituted of optically active molecules due to the inclusion of a chiral center in their molecular structures, then the symmetry elements of the structural environment of each phase are reduced to a single 'polar' two-fold axis of rotation parallel to the layer planes and normal to the tilt axis. This reduced symmetry results in a spontaneous polarization parallel to the layer planes.[22] Another outcome of the reduced symmetry is a tendency for the phase to form a helical distribution of the tilt direction about an axis perpendicular to the layer planes.

The collective structures of the seven 'monoclinic' phases straddle the definitions normally employed in describing *crystallinity*. Three of the phases (C, I, and F) exhibit short range correlations of their molecular positions while the other four (J, G, K, and H) possess long range ordering. Such a simple definition would class the more ordered phases as crystals, however, they still exhibit some properties common to liquid crystals, e.g. miscibility criteria etc. A more complete way of describing this situation is to consider the degrees of freedom (vibration, rotation, and translation) of the molecules, their positional ordering, and their orientational ordering collectively as inter-related factors. Normally an undisturbed crystal possesses long range positional and orientational ordering of its constituent molecules, but the molecules also have vibrational freedom in both stretching and bending modes. When such a crystal melts into a K or H phase, the positional order remains long range, but the orientational ordering and the rotational freedom of the molecules change as they exhibit a rapid reorientational (oscillatory) motion about their long axes. At the transition to the J or G phase, the positional order still remains long range but now the molecules rotate fully, in a coordinated fashion, about their long axes. These two phases (J and G) are therefore analogous to ***anisotropic plastic crystal phases*** in that they have rotational freedom along one axis but not about three axes as in a typical plastic crystal. All four phases (J, G, H, and K), because of their rapid, diffuse molecular motion can be considered as ***orientationally disordered solid phases*** or ***soft crystals***. Further melting provides a transition to the I or F phase which is accompanied with a breakdown in positional ordering, and easier translational motion of the molecules. The orientational ordering in this case takes the form of bond orientational ordering, i.e., the extent of the registry of the hexagonal packing matrix of the molecules and its orientation on passing from layer to layer. Finally at the transition to the C phase, the in-plane positional ordering is lost altogether and only the orientational order of the molecules remains in the form of a director tilted with respect to the layes planes. These three modifications (C, I, and F) can be considered as ***smectic liquid crystal phases***. These related factors can be listed as shown in table 1.

Table 1

Phase Characteristics			Miscibility
structural ordering	orientational ordering	degrees of freedom	Group
1-D density modulation	director†	relatively free translation free rotation	C
3-D hexatic	director† bond orientational ordering	relatively free translation coordinated rotation	I F
2-D crystal (stacked)	director† bond orientational ordering	coordinated rotation	(I)
3-D crystal	director† bond orientational ordering rotational disorder	coordinated rotation	J G
3-D crystal	director† bond orientational ordering reorientational motion	oscillation	K H

† - director is tilted with respect to the layer planes.

Examination of table 1 suggests a possibility that two two-dimensional crystal phases exist. These two phases would differ structurally in the direction of the tilt axis, one being towards the apex and one towards the side of the hexagonal net, in a similar way as they do in I and F, or J and G. Certainly the I phase structure has been described as both a two-dimensional crystal,[6] and a hexatic,[7] which suggests that the two-dimensional crystal phases analogous to hexatic I and F exist. Naturally, if two separate two-dimensional crystal phases exist, they will not be miscible with any of the other phases and would form separate miscibility classes. This would further increase the number of possible ferroelectric phases from seven to nine.

The structural parameters of the seven known "monoclinic" smectic phases that may exhibit ferroelectric properties are given in table 2. Some important points and definitions that arise from this compilation can be listed as follows:

Table 2

	Miscibility grouping	tilt orientation	in-plane correlation length	layer packing order	bond orientational order	layer correlation length	helical tilt orientation	rotational distribution
smectic	C^*	tilted	short range	none	none	none	Yes	free
liquid	I^*	tilt to apex	short range	hexagonal[b]	long range[a]	short range	Yes	6-fold degenerate
crystals	F^*	tilt to side	short range	hexagonal[b]	long range[a]	short range	Yes	6-fold degenerate
	$J^*(G'^*)$	tilt to apex	long range	pseudo[c] hexagonal	long range	long range	No	6-fold degenerate
orientationally	G^*	tilt to side	long range	pseudo[c] hexagonal	long range	long range	No	6-fold degenerate
disordered	H^*	tilted[+]	long range	monoclinic	long range	long range	No	2-fold oscillation
solids	$K^*(H'^*)$	tilted[+]	long range	monoclinic	long range	long range	No	2-fold oscillation

[+] – The tilt direction is either to the short or long edge of the packing matrix, however, it has not been experimentally determined by combined miscibility and structural studies which phase is H and which is K.

[a] – The bond orientational order has to have the helical structuring taken into account for the direction perpendicular to the layers.

[b] – Hexagonal packing in the plane normal to the tilt direction, and the phase is effectively c centered monoclinic.

[c] – The packing is of a distorted hexagonal type in the plane normal to the tilt direction.

1.1 Helical Smectic Phases, Crystal Phases, and Notation

Three of the phases, C^*, I^*, and F^*, are *fluid smectic liquid crystals* and exhibit only short range positional correlations of their optically active molecules. The other four, J^*, G^*, K^*, and H^*, show long range positional ordering and are defined as *orientationally disordered crystal phases*. The *smectic liquid crystal phases* possess a helical distribution of the tilt about an axis perpendicular to the layer planes, but the crystal phases do not possess this structuring because it is suppressed by the long range positional ordering of the molecules. However, the ***orientationally disordered crystal phases*** of optically active materials exhibit *ferroelectric properties* due to the lowered symmetry of the structural environment of the phase. For example the properties of the J* phase are the same as those of a helical phase (C*, I*, or F*) except that its pitch length can be considered as infinite, however, these properties are not exhibited by a J phase whose constituent molecules are not optically active. Consequently the two phases (J and J*) can be distinguished if the asterisk notation is retained in reference to a phase comprised of optically active materials. The helical ordering is only a secondary structural parameter and is a consequence of the material being optically active and of the continuum properties in the fluid phases. In ***the disordered crystal phases*** the suppression of the helical ordering by the long range positional correlations of the molecules can be disrupted, for example in mixtures, and the phases can return to a long pitch length helical structure.[4] In comparison, the orthogonal phases (A and B) possess a higher degree of symmetry and consequently no ferroelectric properties are observed for these modifications. For example, a smectic B* phase possesses identical properties to a smectic B phase, and therefore the asterisk notation becomes redundant in this case.

1.2 Compensated Helical Phases

Two materials exhibiting the same phase but with opposite helical twist senses can be blended together in proportions determined by their helical twisting power to produce a *smectic liquid crystal phase* (C*, I*, or F*) which has an infinite pitch length. The phase can still possess a spontaneous polarization (see later) and be ferroelectric.[5] In this case, since the optical activities of each individual component will not in general be compensated at the same point, the mixture will be optically active even though the much larger optical activity of a helical phase has been removed. Apart from the secondary structure of the helix, the phase has all the attributes of any other ferroelectric smectic liquid crystal except that its pitch is infinite. It is suggested that such a phase, like the *disordered crystal phases* described earlier, should retain the asterisk notation to differentiate it from ideally compensated phases, such as those formed by racemic mixtures.

1.3 Achiral and Non-Chiral Phases

The *disordered crystal smectic phases* can be described as *non-chiral* even though their constituent molecules are optically active while the phase is not. In *smectic liquid crystal phases* of mixtures where the helix has been compromised by compensating components of opposite twist sense, the phase (C^*, I^*, or F^*) can be said to be *achiral* because it was originally derived from helical, optically active phases. In the compensated case the phase can return smoothly to a helical structure in response to a change in its external environment, e.g. temperature, whereas in the case of the *crystal phases* this can only be done by disrupting their internal structures. Examples of materials which exhibit a variety of ferroelectric liquid crystal phases are given in Table 3.

2. Design of Ferroelectric Smectogens

In the following sections the design requirements for ferroelectric smectogens are discussed.

2.1 The synthesis of materials which exhibit tilted and ferroelectric phases.

The first requirement in the synthesis of materials which possess ferroelectric phases is to be able to produce materials which exhibit tilted smectic phases. Many studies have already given guidelines for this initial operation.[8-11] These generally involve the synthesis of materials which possess

(a) an alkyl-aryl-alkyl system

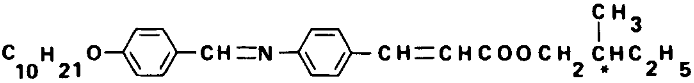
(b) strong terminal lateral dipoles

(c) at least two aromatic rings.

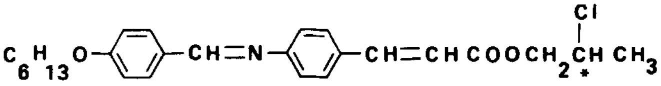
(d) a chiral, center which reduces the symmetry of the phase, and produces the ferroelectric properties.

The formation of ferroelectric smectogens is governed by two related factors; the steric shape of the molecule, and its dipolar character.

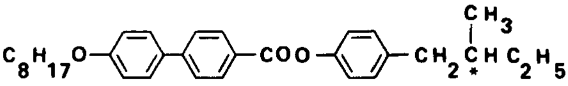
Table 3



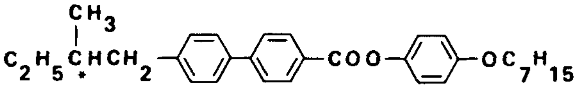
$\text{Iso} \rightarrow S_A \rightarrow S_C^* \rightarrow S_I^*$



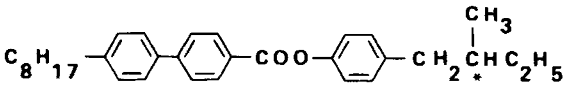
$\text{Iso} \rightarrow S_A \rightarrow S_C^* \rightarrow S_I^* \rightarrow S_J^*$



$\text{Iso} \rightarrow \text{Ch} \rightarrow S_A \rightarrow S_C^* \rightarrow S_I^* \rightarrow S_J^* \rightarrow S_K^*$

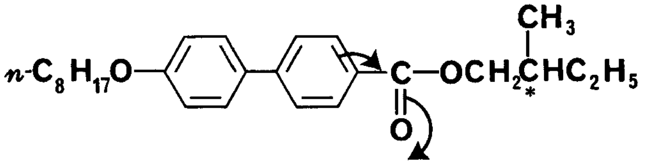


$\text{Iso} \rightarrow \text{Ch} \rightarrow S_C^* \rightarrow S_J^*$



$\text{Iso} \rightarrow \text{Ch} \rightarrow S_A \rightarrow S_C^* \rightarrow S_I^* \rightarrow S_J^* \rightarrow S_G^*$

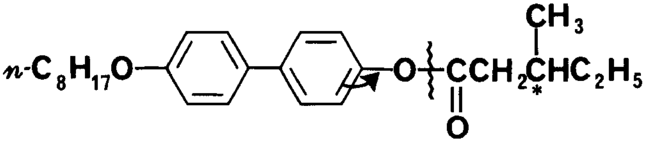
Interactions between these two factors can be divided into a number of subsections, for example, the direction of the dipoles with respect to the overall molecular structure, and how they are coupled to the delocalized electrons of the central aromatic core helps to determine which phase is exhibited. This interaction is illustrated by the two compounds[12]



(I)

$\mathrm{Iso} \longleftrightarrow S_A \longleftrightarrow S_C^*$

and



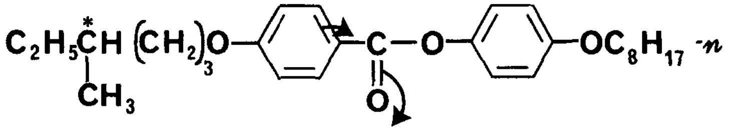
(II)

$\mathrm{Iso} \longleftrightarrow S_G^*$

ester (I)(S_C^*) has its carbonyl function of its terminal ester group conjugated with the delocalized electrons of the biphenyl core, while in compound (II)(S_G^*) this conjugation is disrupted by the ether linkage. It appears that a material in which the π electrons of the core are polarized is more likely to form *smectic liquid crystals* than *disordered crystal phases*.

The length of the terminal chains with respect to the central linkage is another important factor in phase formation. For example, in esters usually one terminal chain, say a dominant alkoxy end, must be at least eight carbon atoms long, while the other must be over four units long before tilted phases are observed.[13,14] In the case of Schiff's bases, however, these numbers are often considerably lower. Furthermore, *crystal smectic phases* commonly occur at shorter chain lengths while the *smectic liquid crystal* phases occur for both short and long chain lengths.[12,14]

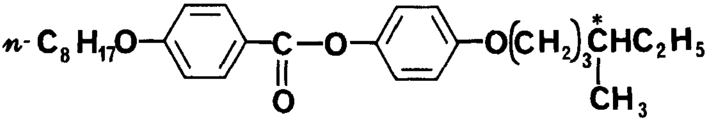
The end of the molecule at which the optical center is positioned in relation to the possible flow direction(s) of the delocalized electrons of the core, which in turn is controlled by the dominant central linkage, also plays an important role in phase formation. Consider the two compounds III and IV,



(III)

$$\mathrm{Iso} \longleftrightarrow \mathrm{Ch} \longleftrightarrow S_C^*$$

and

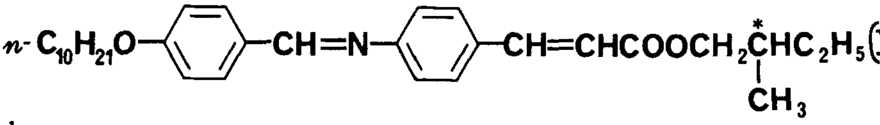


(IV)

$$\mathrm{Iso} \longleftrightarrow \mathrm{Ch} \longleftrightarrow S_A \longleftrightarrow S_C^*$$

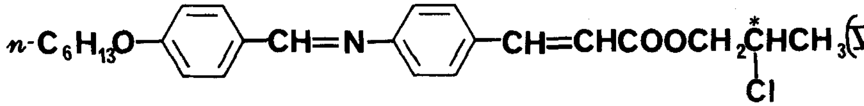
when the optical center is not linked or in close proximity to the polarizable π electrons, as in compound (IV), then an extra phase (S_A) is injected into the phase sequence (also compare Figs. 1 and 2). The injection of an A phase is a useful technique to employ in material design when the alignment of a ferroelectric phase is required to proceed *via* the cooling of a uniaxial smectic A phase.

Finally, chemical and U.V. stability is an integral part of the structure and chemistry of the material. The first ferroelectric crystals described were Schiff's base derivatives with the following structures[15,16]



(V)

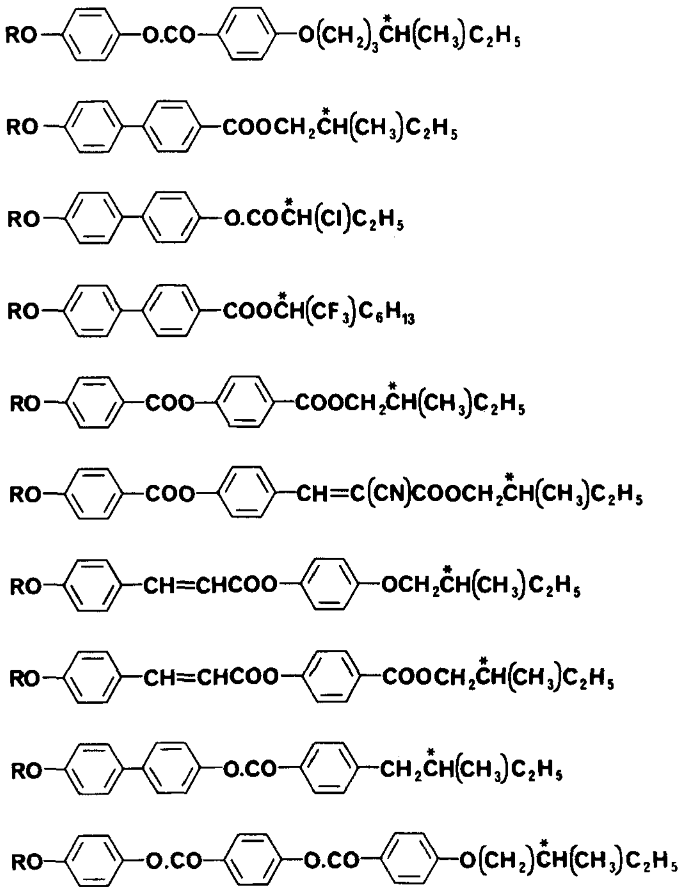
and



(VI)

neither of which is stable for long periods at elevated temperatures in its ferroelectric phases. Esters are generally more stable than Schiffs' bases and for this reason many derivatives of types (I) to (IV) have been prepared.

TABLE 4



R — { n-C_nH_{2n+1} , n ~ 6 – 16 }

The number of aromatic rings included in the structure can be used to vary the transition temperatures of the phases as well as to produce a higher degree of smectic polymorphism. Table 4 lists the types of ferroelectric smectogen that we have synthesized,[12,17] and Figs. 1 and 2 show a comparison between the trends in phase type and transition temperature as a function of increasing terminal alkyl chain length for two isomeric homologous series, these two figures also illustrate some of the points made earlier.

2.2 The Strength of the Spontaneous Polarization

It has been shown that the strength of the lateral dipole associated with the optically active center strongly influences the overall net spontaneous polarization.[2,18] For example, consider structures (V) and (VI), the strength of the spontaneous polarization of (V) is an order of magnitude lower than that of (VI).[2,23] This can be directly related to the strength of the dipole associated with the $C-CH_3$ bond compared to that of the $C-Cl$ bond at the chiral center (provided the enantiomeric excesses of both materials are similar). However, it is not yet clear whether lateral dipoles other than those linked directly to the chiral center have a bearing on the magnitude of the net polarization.

Examination of the structures of materials which typically exhibit ferroelectric smectic phases shows that the optical center is normally at one end of the molecule, often because of the ease of synthesis. In this position it is relatively free to rotate independently of the rest of the molecule which is also rotating, and in particular to the highly sensitive polarizable central core which contains the delocalized π electrons. In this situation the contribution by the core to the dipole associated with the chiral center will be reduced because the lateral dipole of the core will be rotating independently of the asymmetric center and therefore will not contribute greatly to the net resultant dipole. The strength of the spontaneous polarization can be increased considerably by restricting the freedom of rotation of the chiral center in relation to the molecule as a whole. This can be achieved in some sense by moving the branch closer to the core thus creating a direct

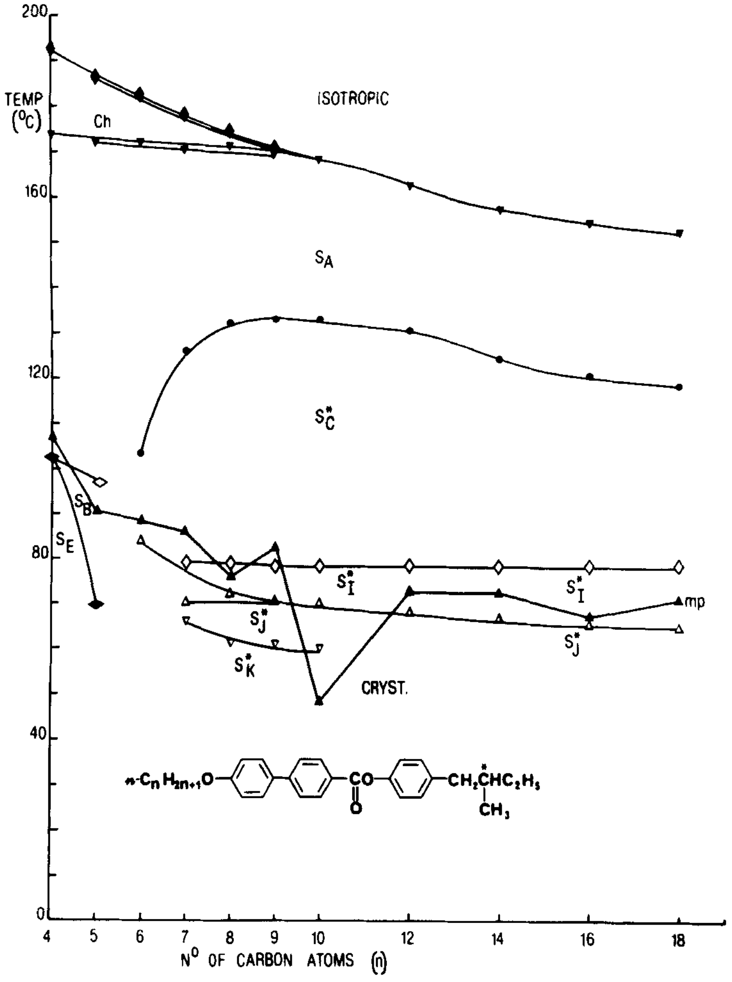


Fig. 1 Plot of transition temperatures against the number of carbon atoms (n) in the n-alkoxy chain of the 4-(2′-methylbutyl)phenyl 4′-n-alkoxybiphenyl - 4- carboxylates; Key: ◆, Ch-I; ▼, S_A-I or Ch; ●, S_C^*-S_A; ◇, $S_I^*-S_C^*$; △, $S_J^*-S_I^*$; ▽, $S_K^*-S_J^*$; ◇, S_B-S_A; ◆, S_E-S_B; ▲, crystal-mesophase.

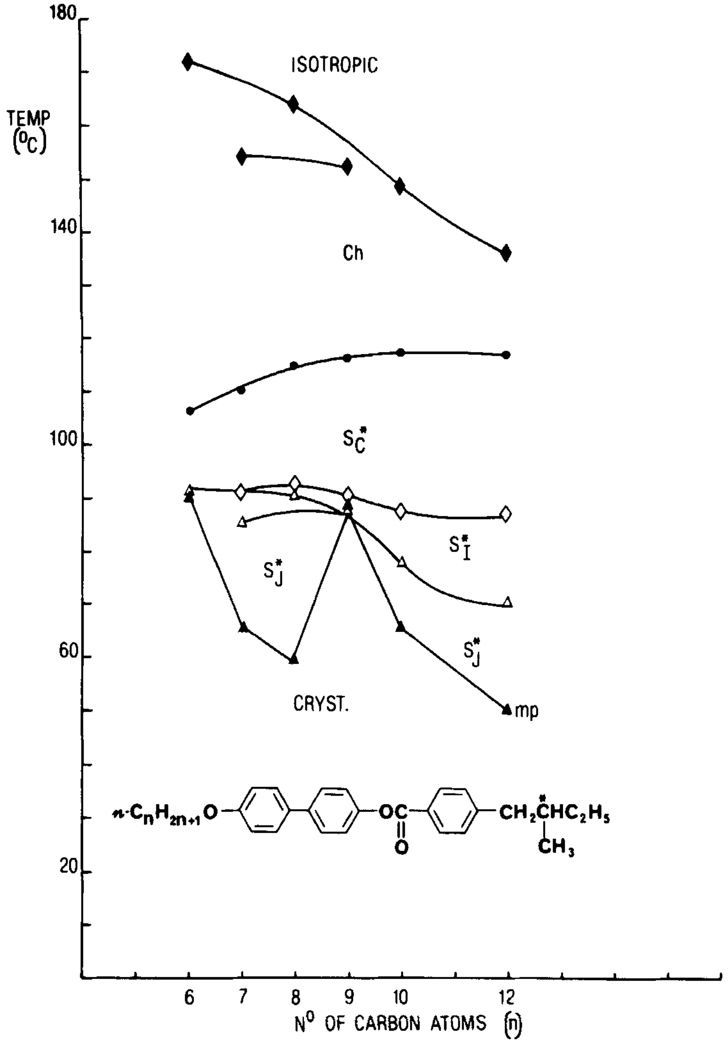
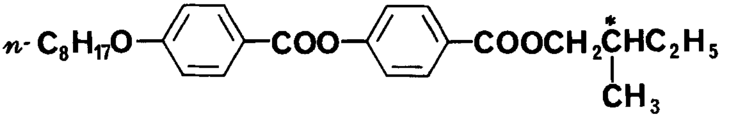
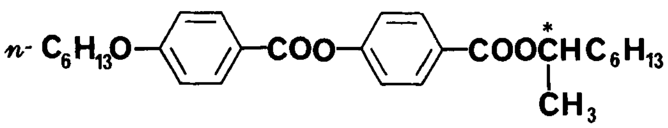


Fig. 2 Plot of the transition temperatures against the number of carbon atoms (n) in the n-alkoxy chain of the 4-n-alkoxybiphenyl 4-(2′-methylbutyl)benzoates; Key: ◆ , Ch-I; ●, S_C^*-Ch; ◇, $S_I^*-S_C^*$; △ , $S_J^*-S_I^*$ or S_C^*; ▲ , crystal-mesophase.

interaction between the two *via* dipolar coupling and restricted rotation. This unfortunately can have detrimental effects on the stability of the ferroelectric phase which is often lost altogether if the chiral center is positioned adjacent to the core. The pitch of a helical phase also becomes shorter as the chiral center is brought closer to the aromatic core, which is unfavorable in applications where the helix needs to be suppressed by surface boundary conditions. For example


(VII)

exhibits A and C* phases while


(VIII)

does not exhibit any phases.

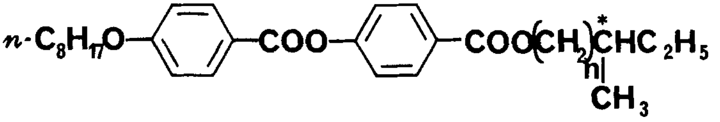
2.3 Stereospecific Properties

The spacial configuration about the asymmetric center of the molecule determines the overall optical activity of the helical phases C*, I*, and F*. When the optical center is moved stepwise along the terminal alkyl chain of the molecule away from the central core there is an odd-even effect, i.e., the helical twist sense alternates from left to right. The same rules[19] that relate the absolute configuration (R and S), the helical twist sense (d(+) and l(−)), and the position along the terminal chain that the chiral center is from the core (odd number of atoms, O, or even number of atoms, E) in cholesterics appear to be valid for smectics. Table 5 gives the relationships between the twist sense and the absolute spacial configuration for smectogens.

Table 5

Right Hand Helix			Left Hand Helix		
absolute config.	chiral center position	twist sense	absolute config.	chiral center position	twist sense
S	E	d	S	O	l
R	O	d	R	E	l

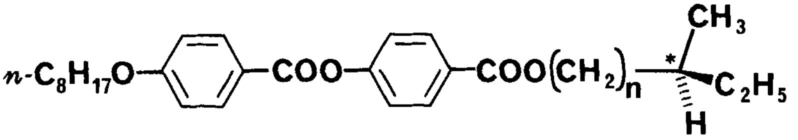
In the case of the homologous series



$n\text{-}C_8H_{17}O-C_6H_4-COO-C_6H_4-COO(CH_2)_n\overset{*}{C}H(CH_3)C_2H_5$

(IX)

as n is increased, the way in which a plane of polarized light is rotated by the helix of the ferroelectric phase alternates from right (d) to left (l), even though the absolute spacial configuration is maintained. The precursor in the synthesis of these materials is S-(-)-2-methylbutan-1-ol, and the extension of the alcohol chain can be achieved without inversion or racemization of the optical center, as shown in Fig. 3. The absolute configuration (S) is maintained throughout the synthetic procedure and esterfication of the alcohols with 4-n-octyloxybenzoyloxybenzoic acid yields the homologous series (IX) which has the absolute structure



(IX)

(S)

where n = 1, 2, 3 etc. The pitch of the phase exhibited by these materials can be varied by mixing members of the series where n is even with those where n is odd, because the tilt direction of the ferroelectric phase is rotated right and then left as n is increased incrementally.

Another interesting point brought out by considering the spacial distribution is when the all-*trans* conformations of the molecular structures associated with the odd and even members are examined. When the chiral center has the same absolute spacial distribution of groups about it, and the resultant dipole of the center is positioned in the same direction, the position of the long axis oscillates back and forth with respect to the incremental change in the value of n, because a conformation change occurs about the

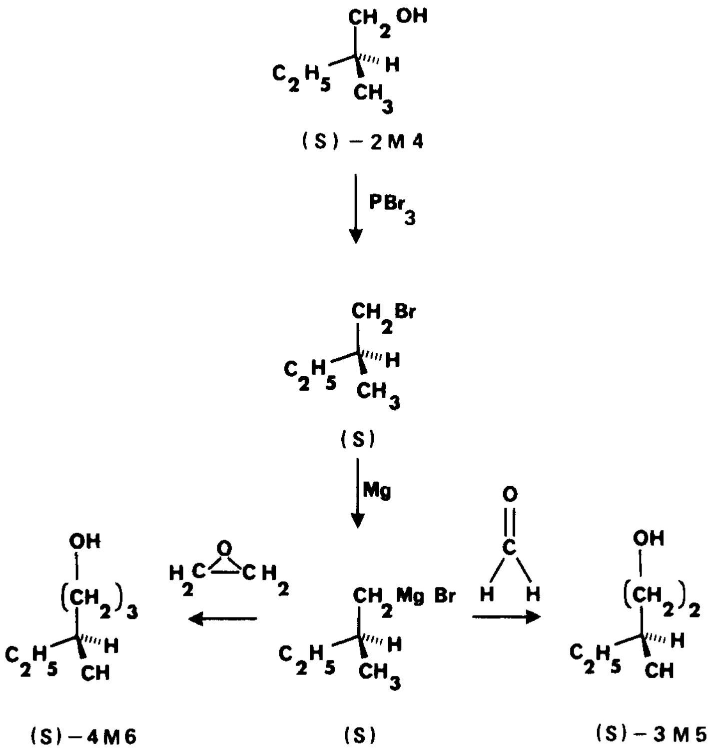


Fig. 3 The synthesis of optically active S-methyl alcohols from S-(-)-2-methylbutanol.

bond between the core and the chain. Alternatively, if the position of the long axis is maintained then the direction of the dipole and the branch associated with the chiral center oscillates back and forth across the long axis as n is increased, see Fig. 4.

Thus, for a given tilt direction, the position of the dipole associated with the asymmetric center for a molecule in its all-*trans* conformation is controlled by the number of atoms the chiral center is removed from the core. The dipolar nature of the chiral center strongly influences the strength of the spontaneous polarization, and therefore its position in relation to the tilt direction will also determine the direction of the spontaneous polarization. As the number of atoms in the spacer group is increased incrementally, not only will the helical twist sense alternate according to the rules given in table 5, but also the direction of the spontaneous polarization will alternate back and forth with respect to the tilt orientation, as shown in Fig. 5, for a given homologous series.

However, unlike the rules that govern the relationship between absolute configuration and helical twist sense; the relationship between the directions of the tilt and the spontaneous polarization cannot be extrapolated from one system to another, but have to be determined experimentally. This is because the dipole direction can change with alterations to the core or to the other groups about the asymmetric center. For example, a group attached to the chiral center can be either an electron donor with a positive induction (+I) effect along the σ framework, e.g. methyl, ethyl, methoxy, etc., or an electron withdrawing group with a negative inductive (−I) effect, e.g., chloro, cyano, fluoro, etc. Thus, the dipole and spontaneous polarization directions for a given absolute spacial configuration will depend on the distribution of electronic charge about the chiral center, see Fig. 6. However, it is still not clear whether it is the dipole direction or the steric shape that directly influences the twist sense. If it is the dipole direction, then such a system will contradict the rules given in table 5. Therefore, the basic rules are incomplete, and the electronic distribution about the chiral center will

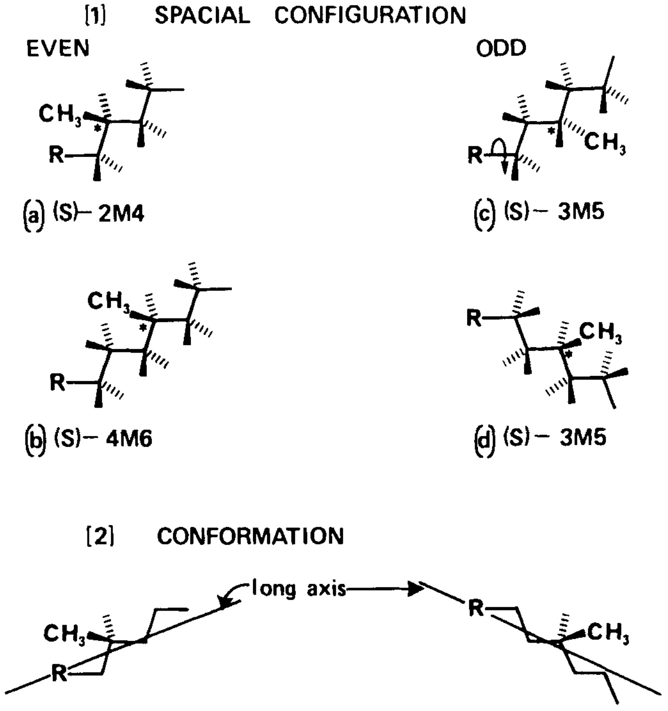


Fig. 4 (a) The spacial configuration about the optical center

(b) The conformation of the groups with respect to the chiral center have to be taken into account in order to define a system fully, i.e., the twist sense related to the direction of the spontaneous polarization.

Experimentally the relationship between the tilt and spontaneous polarization directions can be determined by applying a DC field on the specimen while in its uniaxial phase, and observing which direction the molecules move when cooled into the ferroelectric phase. The tilt direction

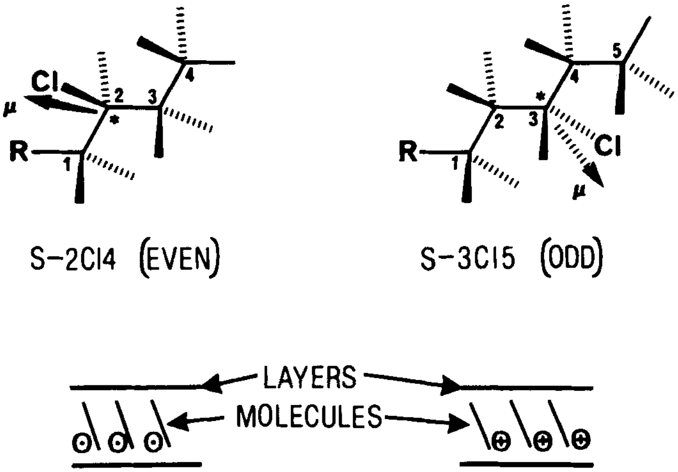
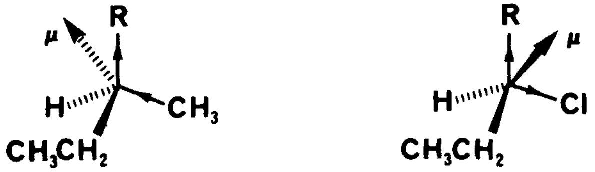


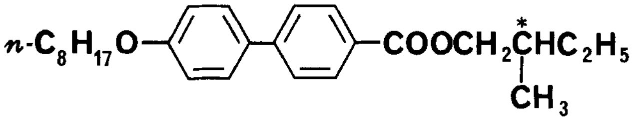
Fig. 5 Alternation of the dipole associated with the asymmetric center with increasing spacer unit length (n) with respect to a given tilt direction.



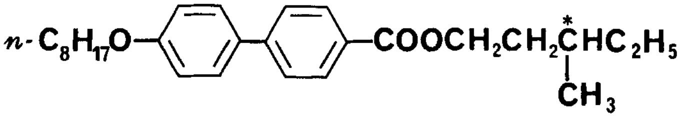
(+I) (-I)

Fig. 6. Electronic and dipole distribution about the chiral center, (a) the effect of electron donating groups, and (b) the effect of electron withdrawing groups. The core is represented by the group R.

of the molecules is opposite to the direction that the sample has to be rotated between crossed polarizers in order to bring it back to extinction when cooled from the uniaxial phase(A) to the ferroelectric phase (C^* etc.). This concept has been intially tested for the following two pairs of materials

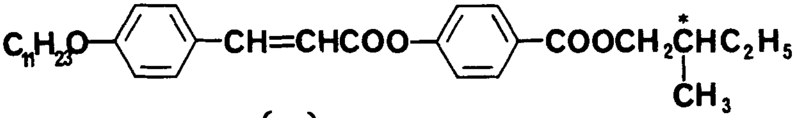


$n\text{-}C_8H_{17}O\text{-}C_6H_4\text{-}C_6H_4\text{-}COOCH_2\overset{*}{C}H(CH_3)C_2H_5$ (X)

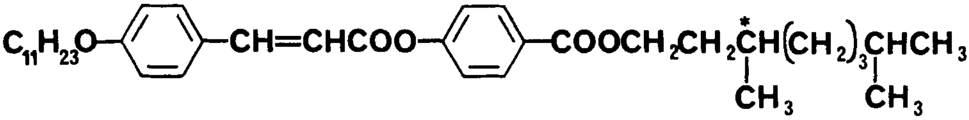


$n\text{-}C_8H_{17}O\text{-}C_6H_4\text{-}C_6H_4\text{-}COOCH_2CH_2\overset{*}{C}H(CH_3)C_2H_5$ (XI)

and



(XII)



(XIII)

which all exhibit S_A and S_C^* phases. Contact preparations between the two pairs of C* phases show that the pitch bands obtained in the focal-conic textures of the individual components disappear in the mixed contact region (see Plate 1). Thus, the pitch of the helix of the C* phase is increased considerably in mixtures of the two compounds, and therefore the two C* phases must have opposite twist senses.

In electric field experiments both phases have their molecules tilting in opposite directions to an identical pulsed voltage of positive polarity (see Plates 2 and 3). The optical contrast of the two halves of the contact preparation are opposite in nature, when one appears light the other is dark. This can only result from the two compounds having opposite tilt directions in an applied field of common polarity. This result confirms that the direction of the spontaneous polarization also alternates, in the same manner as the twist sense, as the chiral center is removed incrementally away from the core.

In applications it is usually necessary to produce eutectic mixtures which exhibit the required phase at room temperature. To obtain a high spontaneous polarization, it is

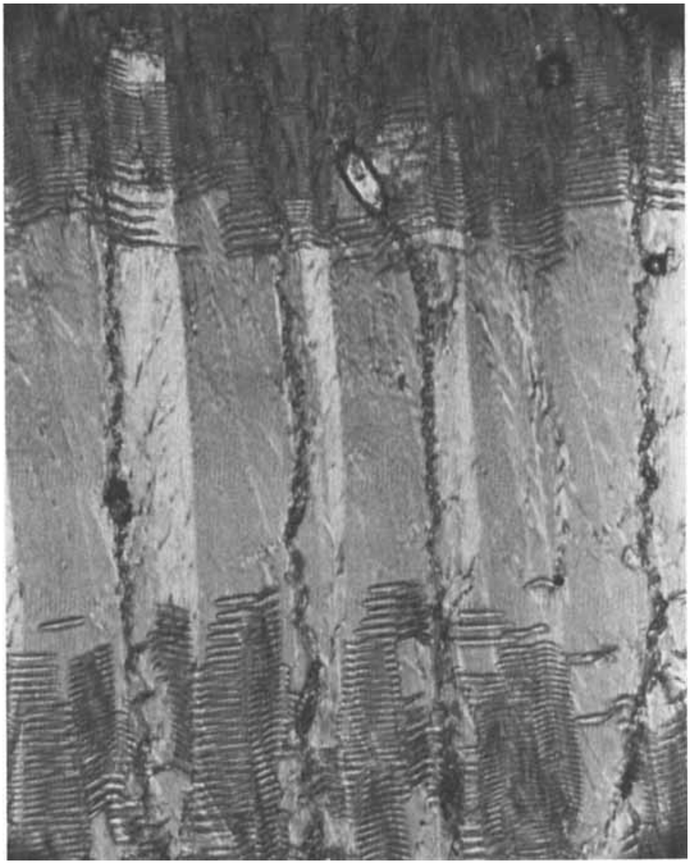


Plate 1: The contact region between compound (XII) (Top) and compound (XIII) (bottom). The two materials have opposite helical twist sense, and in the central region of the plate the pitch bands disappear as the pitch of the mixture is increased.

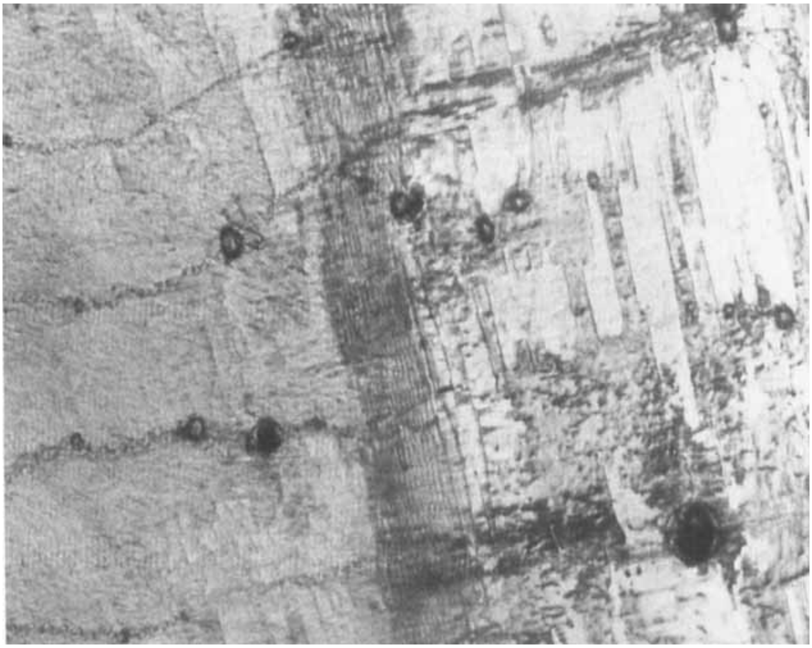


Plate 2: The switched state of the contact region for a DC pulse of +50 volts across a 25 μm cell for the aligned compounds (XII) and (XIII). The two pure materials show different optical contrasts indicting that the relationship between the tilt direction and the spontaneous polarization for (XII) is opposite to that for (XIII).

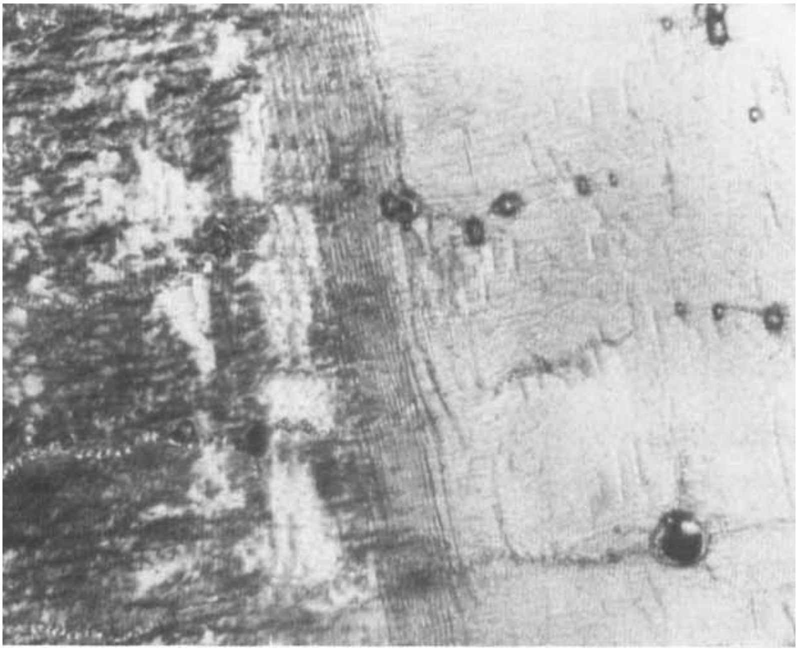


Plate 3: The same area as in Plate 2 except the contact region is subjected to a DC pulse of −50v. The optical contrasts of the two regions are now reversed.

important to mix materials which have the same direction of the polarization, but not necessarily the same twist sense (the opposite is preferable in some cases). However, mixing members of odd with even values of n of the same homologous series will result in a lowering of the net polarization because of the alternation effects.

3. Eutectic Mixtures

3.1 Phase temperature range

An approximation to the melting point of mixtures can be calculated from the Schröder-van Laar equations by using the more complex form:[20]

$$Ti = \frac{\Delta H_{oi} + \Delta H^{tr}_{oi}}{\Delta\frac{H_{oi}}{T_{oi}} + \frac{\Delta H^{tr}_{oi}}{T^{tr}_{oi}}} - R\,\ell n\,Xi:$$

where T_{oi} = melting point of pure component i

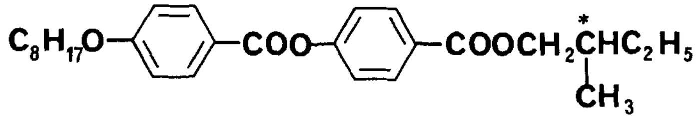
ΔH_{oi} = molar heat of fusion for the component

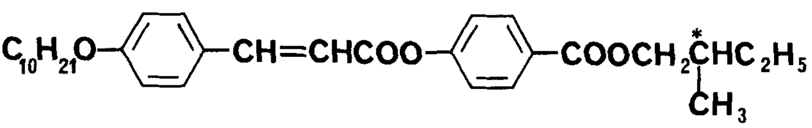
ΔH^{tr}_{oi} = molar heat of transition

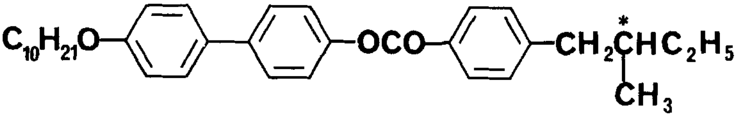
Xi = mole fraction of component i

Unlike nematics it is generally better to mix materials together which do not possess similar molecular structures. This produces an incompatibility in the system which helps to prevent the nucleation process for recrystallization from occurring, and also reduces the melting point of the mixture.

For example, mixtures of two, two and a half and three benzene ring compounds give wide temperature range, low melting, ferroelectric mixtures. e.g

(XIV)  17%

(XV)  55%

(XVI)  28%

$\mathrm{Iso} \underset{97}{\longleftrightarrow} S_A \underset{50}{\longleftrightarrow} S_C$ m.p. 10 Calc. 14

3.2 The Spontaneous Polarization

The spontaneous polarization direction has to be the same for all of the materials in the mixture in order for the resultant of the the lateral components to be maximized, thus creating a large spontaneous polarization.

3.3 Helical Pitch Length

It is necessary to add at least one material of opposite twist direction to a mixture of components of common twist sense in order to vary and increase the pitch of the phase. This is important in devices of the Clark-Lagerwall type[1] where the pitch must be greater than the cell thickness. In this case if the additive is of the same homologous series it will have a similar structure to the other components, but the chiral center should be further from, or closer to, the core by one atom. However, this may also have detrimental effects by lowering the spontaneous polarization because of the odd-even effect on the relationship between the tilt direction and the direction of the spontaneous polarization.

4. Conclusion

In the design of materials suitable for applications it is necessary to take a number of factors into account. These include

(a) the gross molecular shape

(b) the aliphatic to aromatic constitutent ratio and their distribution

(c) The direction of the polarizability of the delocalized electrons

(d) the placement of the chiral center and its relation to helical twist sense

(e) the relationship between the directions of the tilt and the spontaneous polarization.

Acknowledgement

We are grateful for the support of and discussions with Dr. J. S. Patel, Dr. R. Pindak, Dr. J. Budai, Dr. P. E. Cladis, Dr. M. J. Geary, and Dr. A. R. Kmetz.

REFERENCES

[1] N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett., *36*, 899, 1980.
[2] L. M. Blinov, L. A. Beresnev, N. M. Shtykov and Z. M. Elashviu, J. de. Phys., C3, *40*, 269, 1979.
L. A. Beresnev, L. M. Blinov and G. V. Purvanestskas, J.E.T.P. Lett., *31*, 34, 1980.
[3] J. W. Goodby, Mol. Cryst. Liq. Cryst. Lett., *92*, 171, 1983.
[4] D. Coates and G. W. Gray, Mol. Cryst. Liq. Cryst. Lett., *34*, 1, 1976.
[5] L. A. Beresnev, V. A. Baikalov, L. M. Blinov, E. P. Pozhidaev, and G. V. Purvanetskas, J.E.T.P. Lett., *33*, 536, 1981.
[6] J. J. Benatter, F. Moussa, and M. Lambert, J. de Phys, *41*, 1371, 1980.
[7] A. J. Leadbetter, J. P. Gaughan, B. A. Kelly, G. W. Gray, and J. W. Goodby, J. de Phys., C3, *40*, 178, 1979.
[8] J. W. Goodby and G. W. Gray, Mol. Cryst. Liq. Cryst., *48*, 127, 1978.
[9] W. H. de Jeu, J. de Phys., *38*, 1265, 1977.
[10] W. L. McMillan, Phys. Rev. A, *8*, 1921, 1973.
[11] J. W. Goodby, G. W. Gray, and D. G. McDonnell, Mol. Cryst. Liq. Cryst. Lett., *34*, 183, 1977.
[12] J. W. Goodby and T. M. Leslie, Proceedings of 183rd American Chemical Society Meeting, Las Vegas, Nevada, 1982. Liquid Crystals and Ordered Fluids, Vol. 4, Eds. J. Johnson and A. C. Griffin, Plenum Press, 1984, p1.
[13] J. W. Goodby and G. W. Gray, J. de Phys., *37*, 17, 1976.
[14] L. Richter, N. K. Sharma, R. Skubatz, D. Demus, and H. Sackmann, Mol. Cryst. Liq. Cryst., *80*, 195, 1982.
[15] R. B. Meyer, L. Liébert, L. Strzelecki, and P. Keller J. de Phys. Lett., *36*, 69, 1975.
[16] P. Keller, S. Juge, L. Liébert, and L. Strzelecki, C.R.A.S., *282c*, 639, 1976.
[17] T. M. Leslie, to be published in Ferroelectrics.
[18] L. A. Beresnev, E. P. Pozhidaev, L. M. Blinov, A. I. Paulyuchenko, and N. B. Etingen, J.E.T.P. Lett., *35*, 531, 1982.
[19] G. W. Gray and D. G. McDonnell, Mol. Cryst. Liq. Cryst. Lett., *34*, 211, 1977.
[20] D. Demus, Nonemissive Electrooptic Displays, Eds A. R. Kmetz and F. K. von Willisen, Plenum Press, New York and London, 1976, p. 94.
[21] K. Kondo, Y. Sato, K. Miyasato, H. Takezoe, A. Fukuda, E. Kuze, K. Flatischler and K. Sharp, Jap. J. App. Phys., *22*, L13, 1983.

[22] R. B. Meyer, Mol. Cryst. Liq. Cryst., *40*, 33, 1977.
[23] Ph. Martinot-Lagarde, R. Duke, and G. Durand, Mol. Cryst. Liq. Cryst., *75*, 249, 1981.