

PART II

Results and Discussion

Part IIa

Monomers

Pages 33-63

IIa.1	A brief survey of chiral smectic phases
IIa.1.1.1	<i>The ferroelectric-sub phases</i>
IIa.1.2	Influence of molecular structure on mesomorphism
IIa.1.2.1	<i>Variation in the hydrocarbon chain length</i>
IIa.1.2.2	<i>Variation in the core</i>
IIa.1.2.3	<i>Variation in the chiral moiety</i>
IIa.2	Synthesis and characterisation of monomers
IIa.2.1	<i>Liquid crystalline properties of monomers</i>
IIa.3	Physical measurements
IIa.3.1	Spontaneous polarisation
IIa.3.1.1	<i>Measurement of spontaneous polarisation</i>
IIa.3.2	X-ray studies
IIa.3.2.1	<i>Powder samples</i>
IIa.3.2.2	<i>Oriented samples</i>
IIa.3.3	Optical tilt angle
	References

IIa.1 A brief survey of chiral smectic phases

The compounds that form the smectic A (S_A) and smectic C (S_C) phases have fairly rigid and straight aromatic cores. The alkyl chains at the two ends which have the lowest energy in the extended all-trans configuration make an angle with respect to the rigid core. In the S_C phase the chains would prefer to make a small angle with respect to the layer normal, *i.e.*, in Fig. IIa.1, position 2 has higher energy than position 1.¹ It means that there is a rotational bias in the S_C phase. However, because of the mirror plane, there is no net polarisation in the smectic C phase. Introduction of chirality into the system, either by doping a compound showing S_C phase with a chiral material or by integrating a chiral group into the molecule, breaks the mirror plane symmetry leading to the formation of S_{C^*} phase. In Fig. 1.5, the molecular dipole now can point out of or into the plane of the paper with equal probability and there is a quadrupolar symmetry. We get polarisation if the dipoles are rigidly attached to chiral centres in the molecule. If $\vec{P}$ is along $\vec{k} \times \hat{n}$, where $\vec{k}$ is a unit vector along the layer normal and $\hat{n}$ the director, $\vec{P}$ is considered to be positive and when it is in the opposite direction, it is considered to be negative.

In practice, $\vec{P}$ is found to be negative in most of the ferroelectric liquid crystals. These are fluid ferroelectrics with ferroelectric polarisation in the plane of the fluid layers. Polarisation measurements indicate that the effective dipole moment P , per molecule is quite small ($P \cong 10^{-2}$ Debye). This is due to a weak polar bias in the rotation of the molecules around their long axes in S_{C^*} phase. The dipolar energy ($P_m \times 2/a \cong 10^{-25}$ J), where a is the intermolecular distance, is much smaller than the thermal energy $k_{BT} \cong 10^{-21}$ joules. This means that the dipolar interactions do not produce the transition from S_A phase to S_{C^*} phase. The ferroelectric polarisation $\vec{P}$ is merely due to

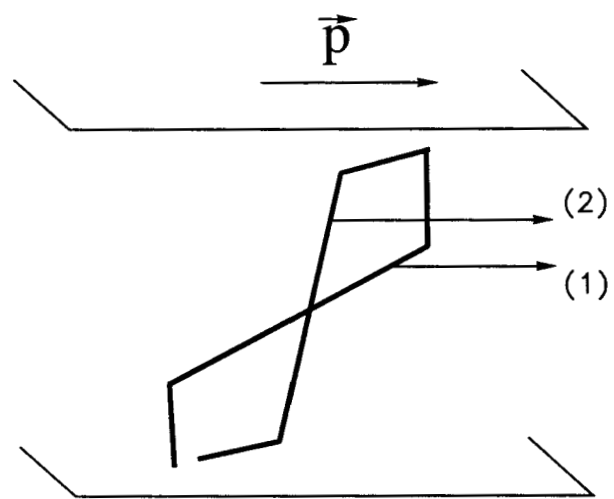


Fig.IIa.1 Position 2 has higher energy then position 1 (after N.A. Clark.¹⁾)

the symmetry of the C* phase. Hence the primary order parameter in the S_A to S_{C^*} phase transition is the tilt angle as in the case of S_A to S_C phase transition of a non-chiral substance. The polarisation $\vec{P}$ is only a secondary order parameter.

In the S_{C^*} phase the tilt direction twists around the layer normal, resulting in a helicoidal structure. The polarisation $\vec{P}$ which is coupled to the tilt also twists around the helical axis $\vec{z}$ (Fig. IIa.2). The polarisation averages out to zero when the helix makes one full 360° turn. Hence, in a macroscopic undisturbed sample which is free from any of the external forces, the polarisation averages to zero. However, if the helix is unwound by external forces such as surface interactions or by compensating the helix in a mixture, the phase will have a net non-zero polarisation. It is because of this reason that the S_{C^*} phase has often been described as helielectric.

Ever since the first ferroelectric liquid crystal synthesised by Meyer *et al.*,² many properties of these ferroelectric liquid crystals have been investigated as they have some advantages over nematic liquid crystals in display applications. Based on an argument similar to that for ferroelectricity in chiral smectic liquid crystals, Garoff and Meyer^{3,4} predicted the existence of the electroclinic effect in the smectic A phase of a liquid crystal composed of chiral molecules. In this phenomenon, by applying an electric field ' E ' parallel to the smectic layers, a molecular tilt is induced relative to the layer normal in a plane orthogonal to E .

IIa.1.1.1 The ferroelectric-sub phases

The antiferroelectric $S_{C_A^*}$ phase and other sub-phases such as ferrielectric $S_{C_\gamma^*}$ and $S_{C_\alpha^*}$ phases were discovered by Chandani *et al.*^{5,6} in 4-(1-

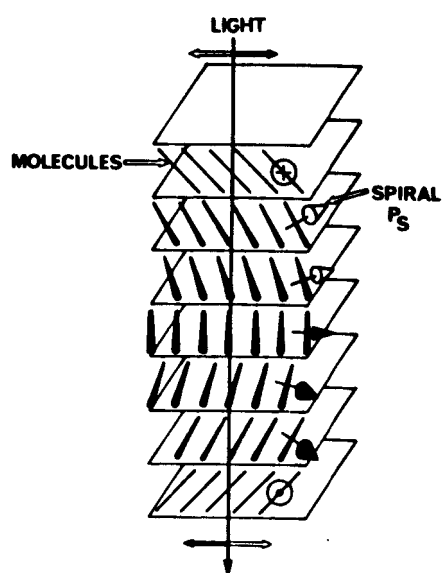


Fig.IIa.2

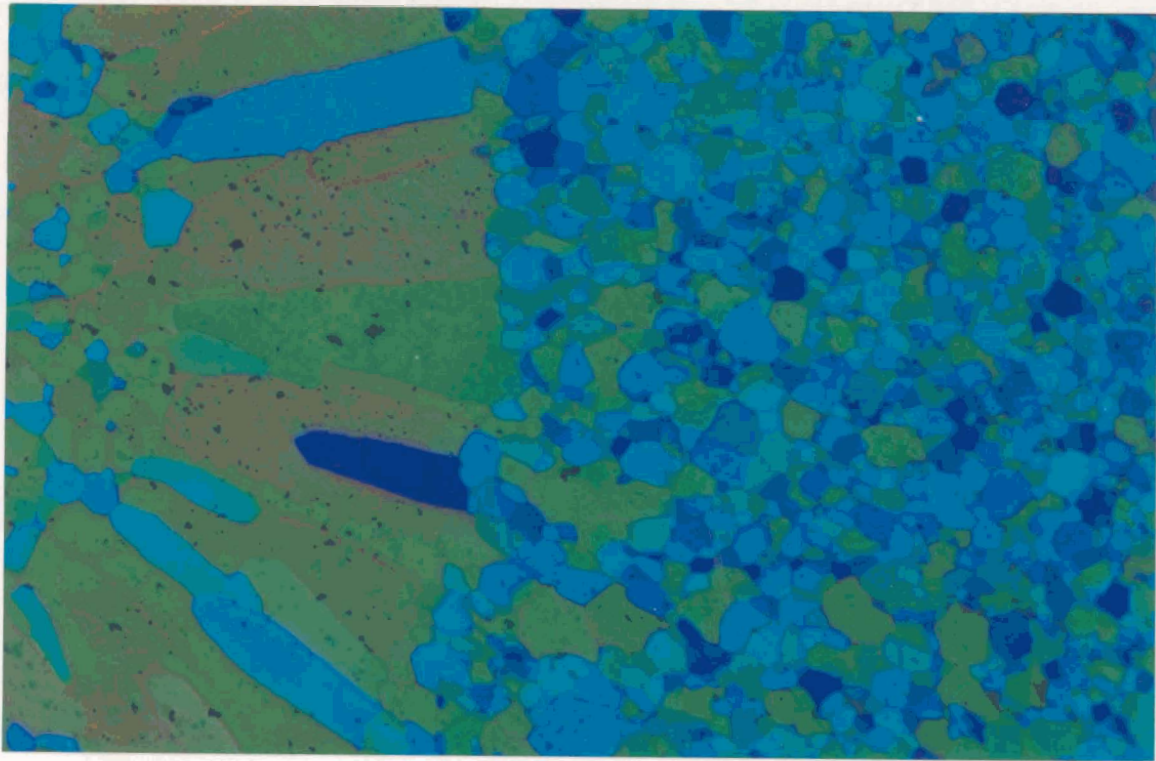


Plate IIa.1 Photomicrograph of sample (K-4) showing Blue phase.

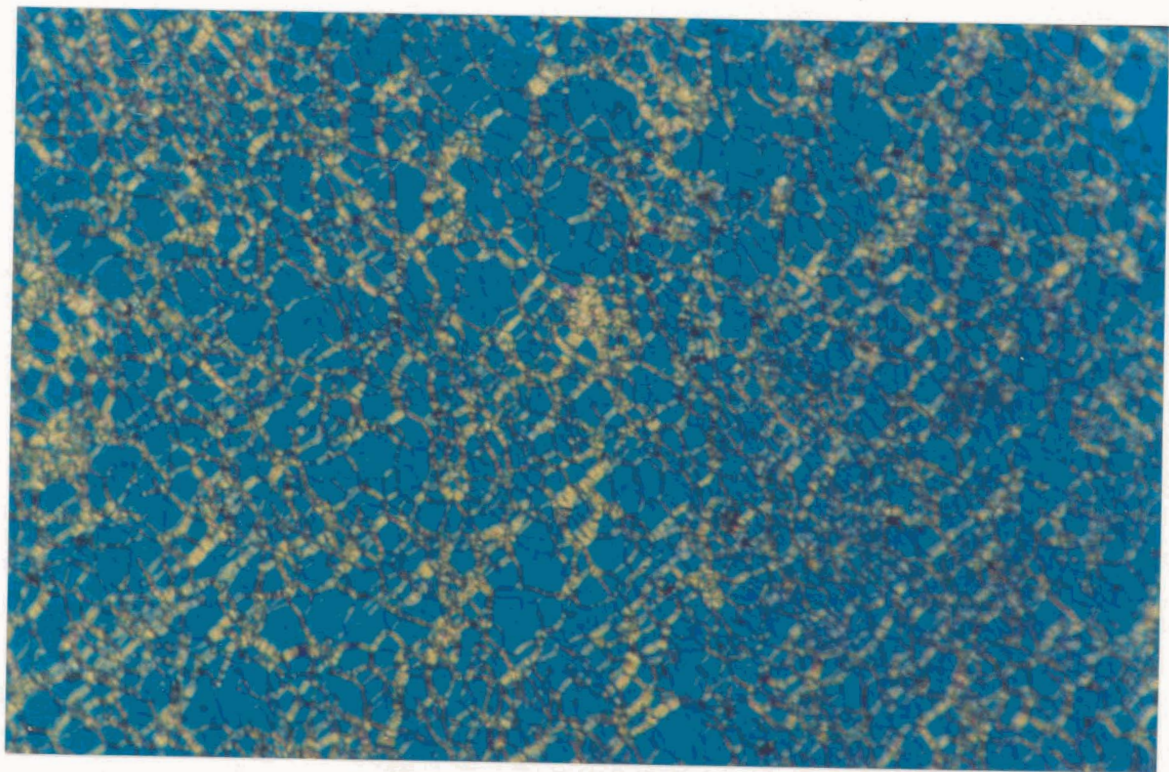


Plate IIa.2 Photomicrograph of sample (K-4) showing Cholesteric phase.

methylheptyloxycarbonyl) phenyl 4'-octyloxybiphenyl 4-carboxylate (MHPOBC). In the antiferroelectric phase, molecules in adjacent layers are tilted in opposite directions, as a result of which, the spontaneous polarisation is averaged to zero for the bulk unwound antiferroelectric phase, in a zero electric field. In the ferroelectric phase molecules are tilted in opposite directions in a random way and because of this random arrangement there is a residual spontaneous polarisation. The mesophase observed by Levelut et al.,⁷ designated as 'Smectic O' phase, in 1-methylheptyl terephthalidene bisarninocinnamate, was **infact** the same as the antiferroelectric phase observed in MHPOBC.

Antiferroelectric phase shows tristable switching from ferroelectric phase to antiferroelectric phase and back to ferroelectric phase, in an electric field, while a ferroelectric phase exhibits tetra-stable switching under an electric field. Hence, these materials can be utilised for fast switching display device **applications**.⁸ The structure of $S_{C\alpha}^*$ phase is not yet very clear though a large number of models have been proposed and it is now known to be **helicoidal**.⁹

IIa.1.2 Influence of molecular structure on mesomorphism

While discussing the structure-mesophase relationships of the chiral mesogens, particularly those exhibiting S_C^* phase, a mesogen can be divided into three parts (Fig. IIa.3), viz., the tail, the core and the chiral group, and the influence of each on the liquid crystalline behaviour is discussed in the following sections.

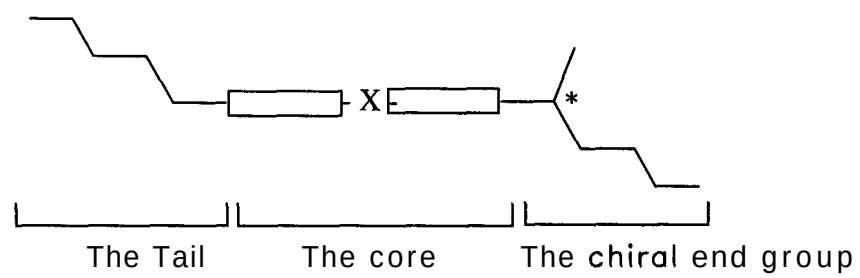


Fig.IIa.3 Schematic figure showing various parts of a chiral mesogen.

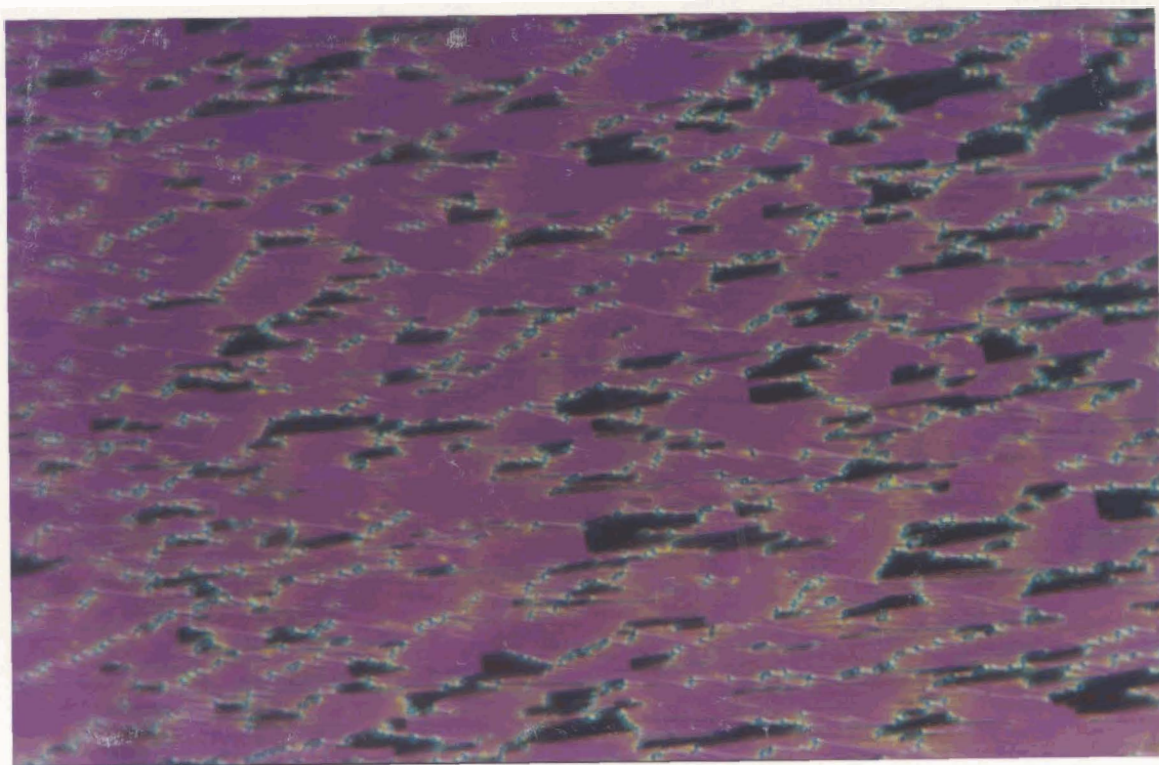


Plate IIa.3 Photomicrograph of sample (A-8) showing Smectic A (partially aligned) phase.

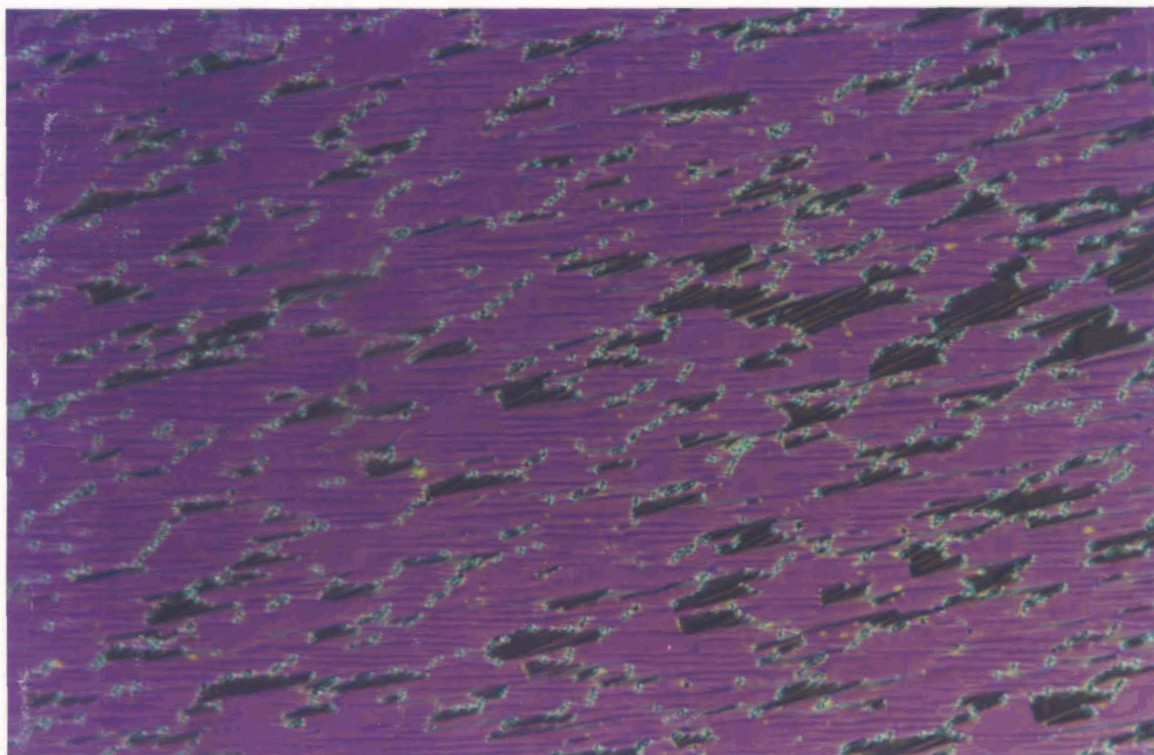


Plate IIa.4. Photomicrograph of sample (A-8) showing $S_{C\alpha}^*$ (partially aligned) phase. Note the dark lines along the alignment direction.

IIa.1.2.1 Variation in the hydrocarbon chain length

Gray and his co-workers^{10,11} have shown that a smooth curve relationship exists while plotting the mesomorphic transition temperatures, the enthalpies and entropies of transition versus the alkyl chain length, for sufficiently large number of homologous series," while the melting points show no regularity. In a chiral series exhibiting smectic phases, the higher homologues tend to exhibit the S_{C^*} phase. In many series of compounds the thermal stability of the S_{C^*} phase is found to increase with increasing number of carbon atoms in the chain.¹² This increase per methylene unit becomes less and less as the chain length increases. However, exceptions to this general trend are known."

Janulis *et al.*¹⁴ replaced the hydrogen atoms in the chain by fluorine atoms and observed an increase in the melting points and a reduction in the thermal stability of the S_{C^*} phase. It was shown by Kelly *et al.*¹⁵ that introduction of a double bond at the terminal end of the chain not only causes a depression in the melting points but also results in the reduction of thermal stability of the S_{C^*} phase. The spontaneous polarisation doesn't show a general trend unlike the thermal stability or the transition temperatures. Its value can increase or decrease as we go along a homologous series.^{16,17}

IIa.1.2.2 Variation in the core

Introduction of an ether linkage between the core and the hydrocarbon chain increases the thermal stability of the S_{C^*} phase.^{18,19} However, little change in the value of spontaneous polarisation was observed.²⁰ The enhancement of the thermal stability due to ether linkage could be attributed to the increased lateral dipole moment. And

this being distant from the chiral centre, the value of spontaneous polarisation is unaffected. Kitamura *et al.*²¹ have reported an example where a monotropic S_{C^*} phase and an enantiotropic S_A phase observed in the alkoxy compound are totally suppressed in the analogous **alkyl** compound, which was found to be non-mesogenic. When an alkoxy group in a compound exhibiting a monotropic S_{C^*} phase and an enantiotropic S_A phase was replaced by an alkanoyloxy group,²² the latter exhibited enantiotropic S_{C^*} phase with an increased thermal stability and an additional ferroelectric phase below the S_{C^*} phase. In lieu, the S_A phase had vanished. This change generally brings about an increase in the thermal stability of the S_{C^*} phase.¹⁹

Inversion of centrally situated ester linkage has dramatic effects upon the phase sequences.^{12,19,20,23,24} It was observed that whenever the chiral moiety is in conjugation with the ester group linked to the core, the S_{C^*} phase goes over to the N^* phase and when it is not, the S_{C^*} phase goes over to the S_A phase on increasing the temperature.¹⁹ When an ester was replaced by a thioester, the thermal stability of the S_{C^*} phase was found to increase.¹⁴ The replacement of central -COO- linkage unit by a -CH₂O- group causes the S_{C^*} thermal stability as well as the value for spontaneous polarisation to decrease.²⁵

When an aromatic ring from the core was substituted by a cyclohexyl ring the polarisability gets reduced and often the S_{C^*} phase disappears **altogether**.^{12,15} A change from cinnamoyloxy to α -methylcinnamoyloxy moiety lowers the mesophase transition temperatures.²⁶ In some cases the value of spontaneous polarisation also gets reduced considerably.²⁷ Similarly, α -chlorocinnamoyloxy group reduces the mesophase temperatures and the α -cyano group increases the melting point, while reducing the thermal stability of the S_{C^*} phase.²⁸

Introduction of a nitrogen atom in the phenyl ring affects the S_C^* phase thermal stability depending on the position of the nitrogen atom in the ring.²⁹ A lateral substituent on a phenyl ring can affect the breadth as well as the lateral dipole of the molecule. Hence it can play a major role in influencing the thermal stability as well as the spontaneous polarisation of the S_C^* phase. If the polar groups are accommodated within the rotational volume of the molecule so that they do not increase the breadth then they tend to stabilise the smectic phases.³⁰ Thus, when a hydroxyl group was substituted on the benzene ring in such a way that it can form an intramolecular hydrogen bond with a carbonyl group³¹ or nitrogen atoms of the benzylideneamino,^{29,32} or benzalazine group,²⁷ it was found to favour the S_C^* phase as well as increase the value of spontaneous polarisation.³³ The same authors have reported the formation of S_C^* and S_A phases instead of the N^* phase, present in the unsubstituted parent compound.

When a halogen was introduced on the phenyl ring *meta* to a carbonyl group, the value of spontaneous polarisation increases, however, if this halogen was present at the *ortho* position to a carbonyl group the value was found to decrease.^{20,34} This has been attributed to the fact that the carbonyl and the halogen groups are likely to lie in opposite directions due to electrostatic repulsion, which, effectively reduces the dipole acting at the chiral centre.

The effect of introduction of a fluorine atom at various positions in compounds exhibiting the S_C^* phase has been studied by Gray *et al.*³⁵ The effect of mono-, di-, and tri-fluorination in many phenyl and biphenyl carboxylates have been investigated by Chambers *et al.*³⁶ The S_C^* phase seems to be a predominant phase in these compounds.

IIa.1.2.3 Variation in the chiral moiety

Studies by varying the chiral moiety are mainly directed towards achieving relatively high values for spontaneous polarisation. An increase in the dipole moment at the chiral carbon atom was found to result in an increase in the value of the spontaneous polarisation. This has been observed in compounds in which a methyl group was replaced by a chloro group.³⁷ It has been observed that the thermal range of the S_{CA}^* phase increases in compounds in which a methyl group was replaced by a trifluoromethyl or a pentafluoroethyl group.⁸ In this case there was a direct transition from S_A phase to S_{CA}^* phase. An epoxy group³¹ was also found to enhance the value of spontaneous polarisation; on the other hand an ethoxy group was not as effective.³⁹ When methylene groups were introduced in between the chiral centre and the core, the value of spontaneous polarisation was found to decrease.^{32,40} This has been attributed to the weakening of the interactions between the core and the chiral centre. This however has little effect on mesomorphism.⁴¹ The helical twist present in the S_{C^*} phase flips from one handedness to the other along a homologous series obtained by introduction of methylene units between the chiral centre and the core.⁴²

The sign of optical rotation and the direction of spontaneous polarisation also alternates. However, Otterholm *et al.*³² have synthesised some compounds where this odd-even effect on the sign of polarisation related to the chiral centre moving away from the core of the molecule is not observed. Reducing the distance between the core and the chiral centre results in the reduction of the pitch.⁴³

Goodby *et al.*⁴⁴ have studied the effect of damping the motion of the chiral centre and its effect on polarisation. They observed that as the terminal chain was extended on the external side of the chiral centre the rotational motion of the chiral

group was restricted which resulted in an increase of the value of polarisation. This damping also enhances the steric repulsive effects and depresses the liquid crystalline phase.

Yoshino *et al.*⁴⁵ have synthesised compounds in which the chiral moiety is flanked by two ester groups and by an ester and an ether linkage respectively. The value of spontaneous polarisation in the latter compound was found to be four times the value of the former. This has been explained by considering the relative orientation of bond moments around the chiral carbon atom. Geelhaar⁴⁶ has reported that, when the 2-methylbutyl group in trans-1(4''-n-alkoxybiphenyl)-4-(2-methylbutyl)-4-cyanocyclohexane attached to the cyclohexane ring is replaced by methyl isopropyl ether, isopropyl acetate or isopropyl pentanoate, the value of spontaneous polarisation increases gradually. For the last compound the melting point gets considerably depressed and a wide temperature range for the S_{C^*} phase was obtained.

From the analysis of ^{13}C NMR spectra and the relaxation times of the carbon atoms, Yoshizawa *et al.*⁴⁷ observed that the rotational frequency of the chiral carbon atom does not change much during transition from S_A to S_{C^*} phase. However, the mobility of the polar group adjacent to the chiral carbon atom (carbonyl in this case) decreases remarkably during the phase transitions. Generally, the enantiomers have identical melting points,⁴⁸ and the same appears to be true for mesomorphic transitions as well.⁴⁹ In S_{C^*} phase the compounds of opposite absolute configurations form helices of opposite twists (handedness) and have polarisation vectors pointing in opposite directions but of same magnitude.⁴² The racemates differ by a few degrees in the mesomorphic transition temperatures as compared to the enantiomers and have non-helical and non-ferroelectric phases. Goodby and Chin⁵⁰ have reported that chirality by

itself can induce additional ferroelectric phases below the S_C^* phase to occur in pure chiral compounds which need not be present in the racemic mixture.

IIa.2 Synthesis and characterisation of monomers

All the monomers synthesised were mesomorphic. The transition temperatures along with their associated enthalpies where ever measurable, are given in **Tab.IIa.1** to **Tab.IIa.4**. The sub-phases could be detected using the highest sensitivity available on the DSC-7 instrument. A DSC thermogram for compound N-8 is shown in **Fig. IIa.4**, and **IIa.5**. The newly synthesised ferroelectric materials, displayed the novel antiferroelectric phase behaviour also.

The synthesis of these compounds were carried out according to the schemes shown in **Figs. IIa.6** to **IIa.11**.

The naphthalene portion of the target material was prepared starting from 2-methoxynaphthalene (**Fig.IIa.6**). This compound was acetylated using anhydrous aluminium chloride in carbondisulphide. The 2-acetyl 6-methoxynaphthalene obtained was oxidised to the corresponding carboxylic acid by using sodium hypobromite, and then demethylated with aqueous 48% hydrobromic acid to give 6-hydroxy 2-naphthoic acid, which was protected as ester by refluxing with ethanol and a small amount of concentrated sulphuric acid as catalyst. The free phenol was condensed with ω -alkene alcohol by using diethylazodicarboxylate and triphenylphosphine following a procedure described by Mitsunobu and Eguchi.⁵¹ The acid was then deprotected by refluxing in aqueous alkaline medium.

The 3-chloro 4-benzyloxybenzoic acid portion of the target compound was prepared from *ortho*-chlorophenol (**Fig.IIa.7**), which was acetylated with

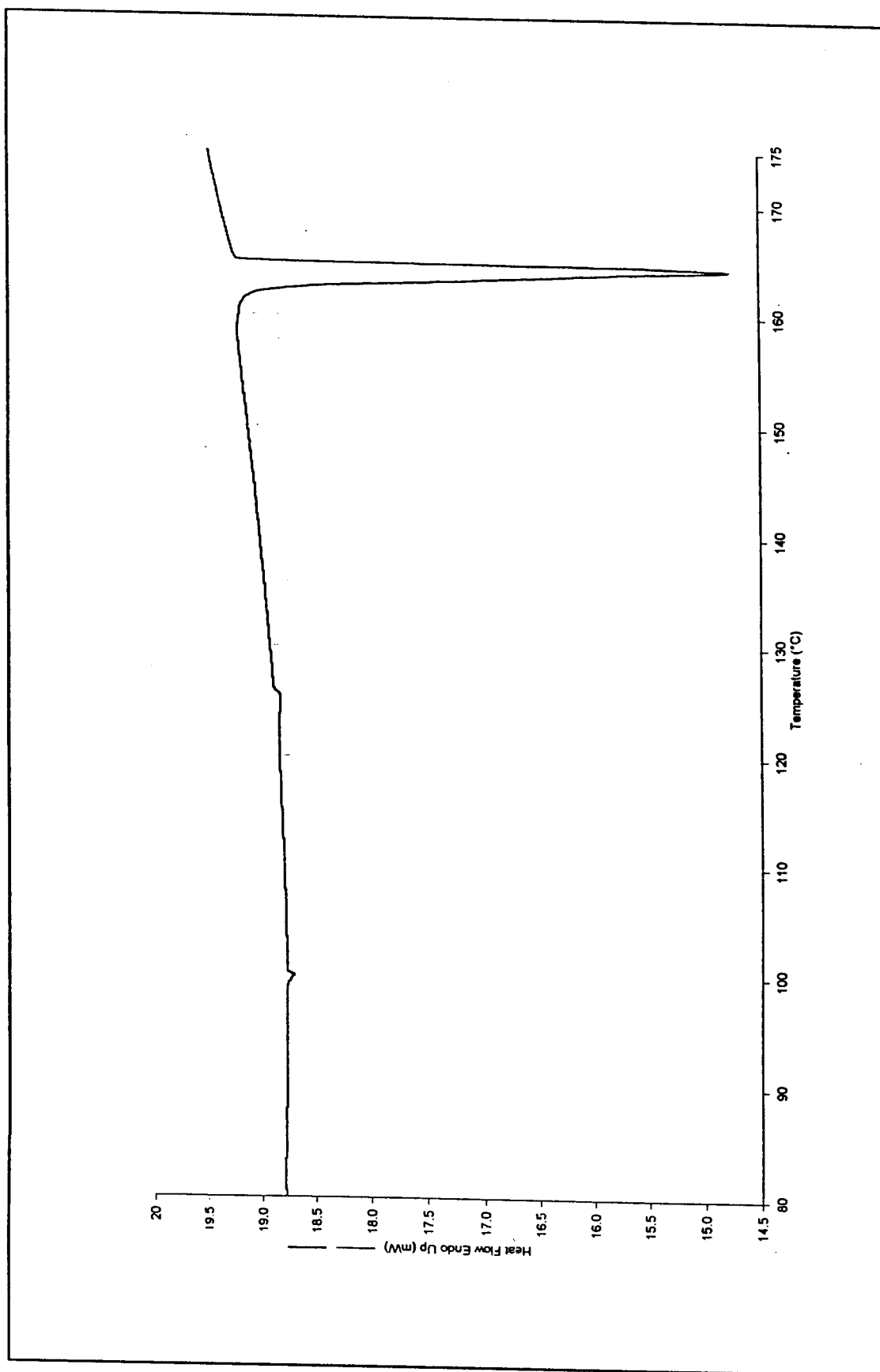


Fig.IIa.4

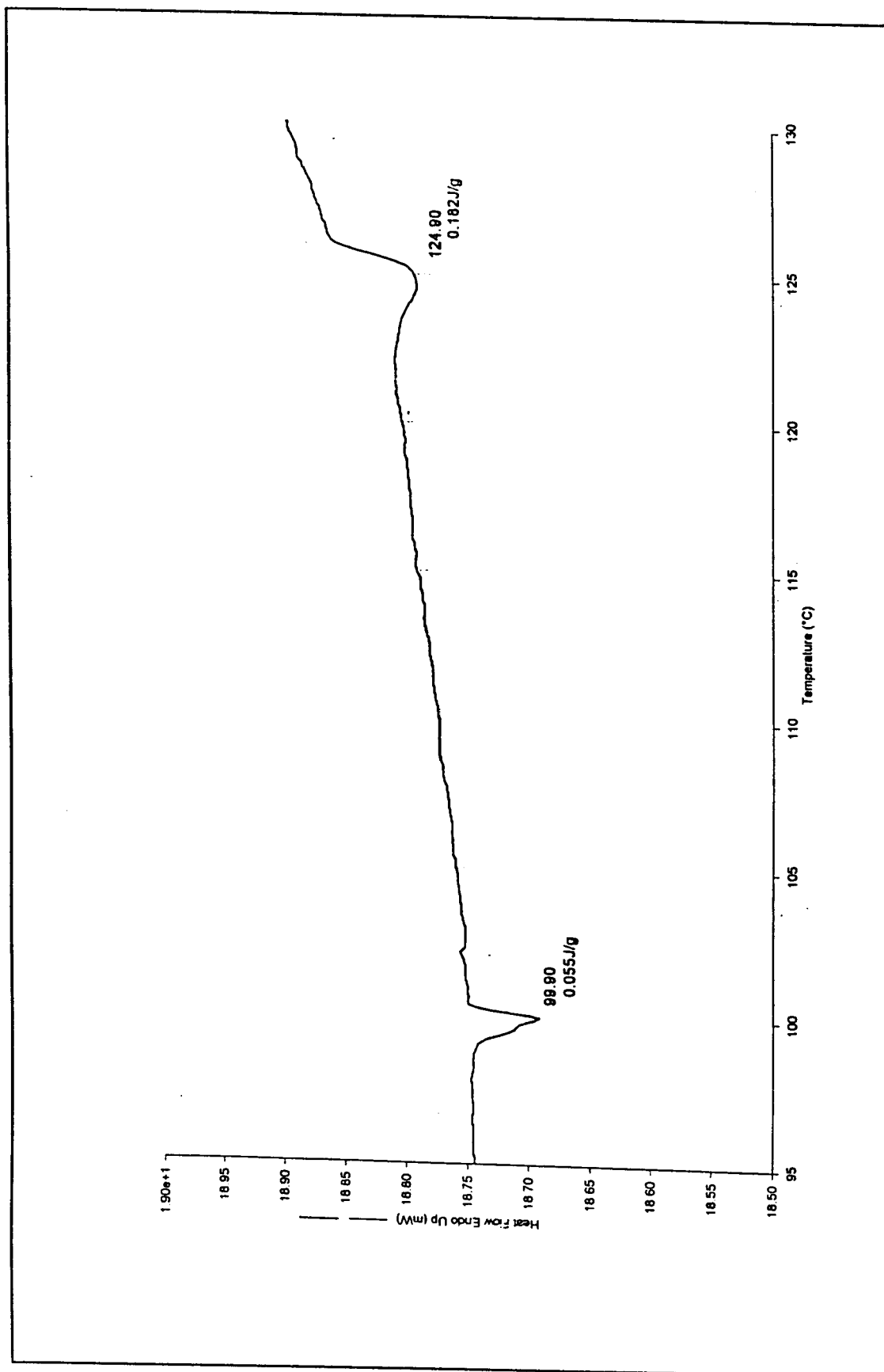


Fig.IIa.5

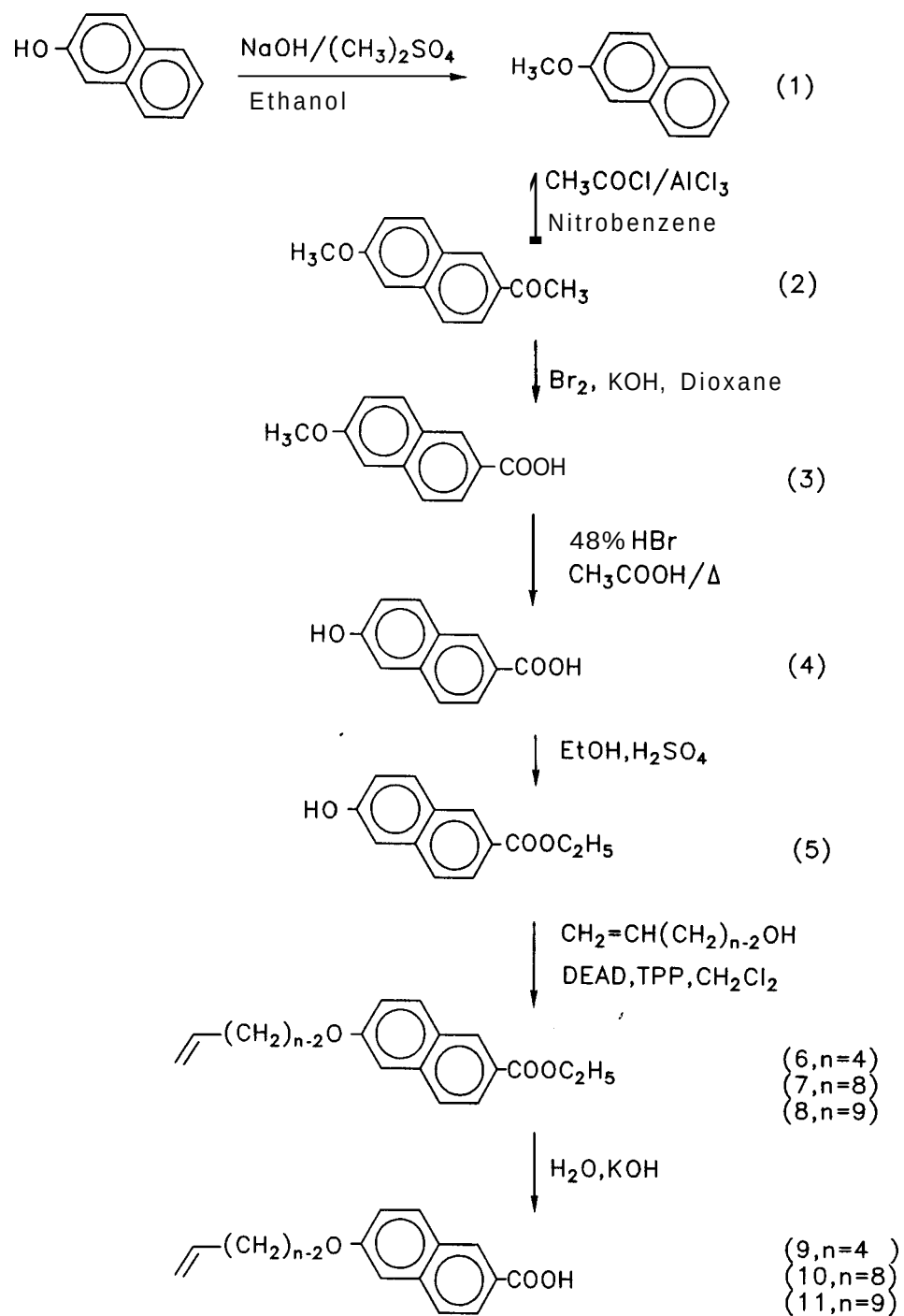


Fig.IIa.6

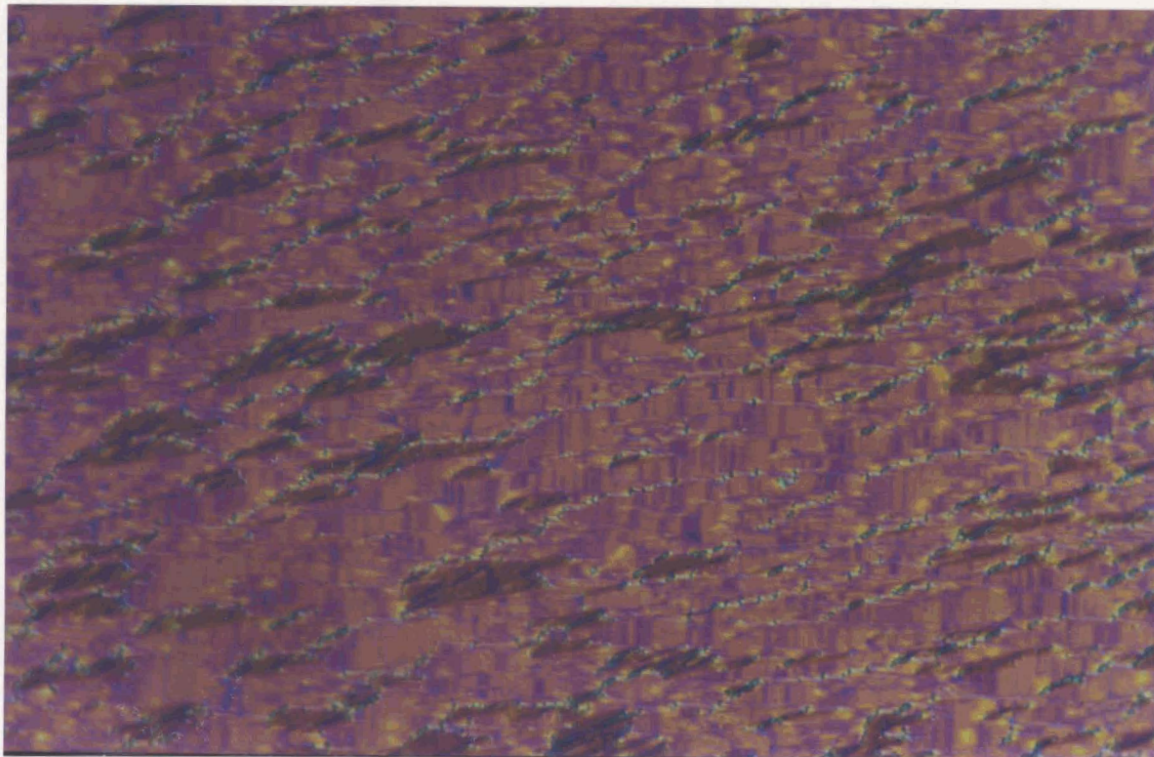


Plate IIa.5 Photomicrograph of sample (A-8) showing S_{C^*} (partially aligned) phase. Note the small lines perpendicular to the alignment direction.

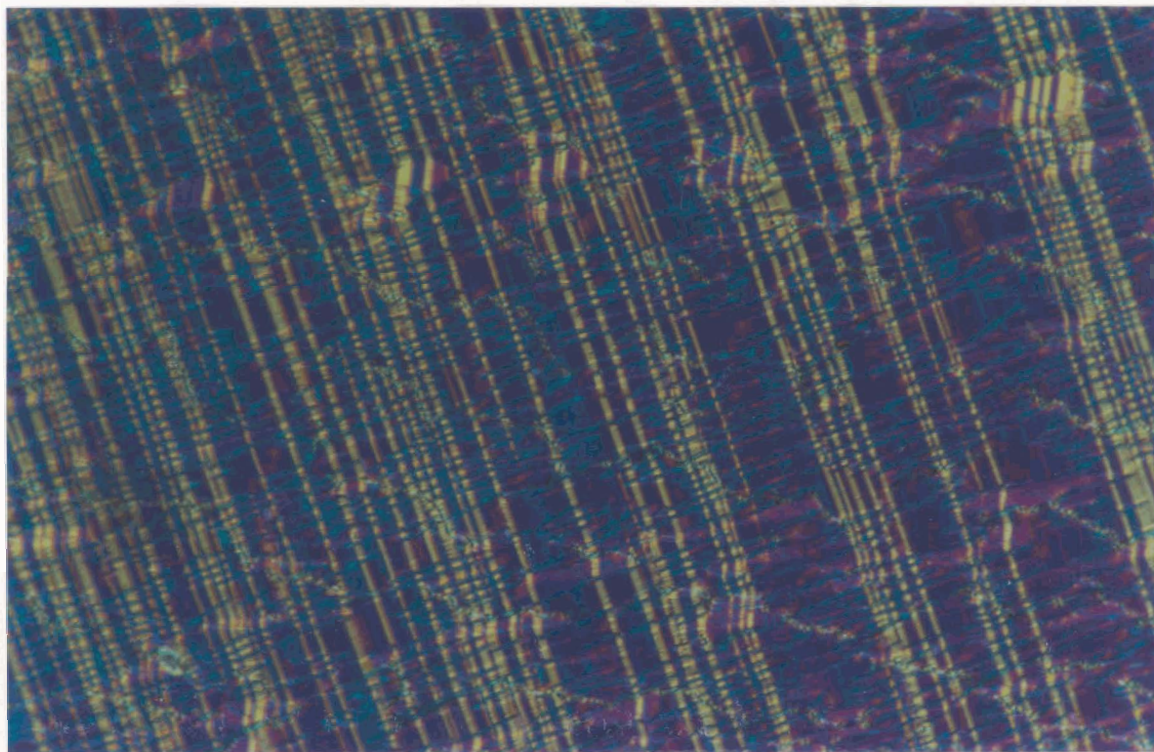


Plate IIa.6 Photomicrograph of sample (A-8) showing $S_{C_A^*}$ (partially aligned) phase. Note the long bright lines perpendicular to the alignment direction.

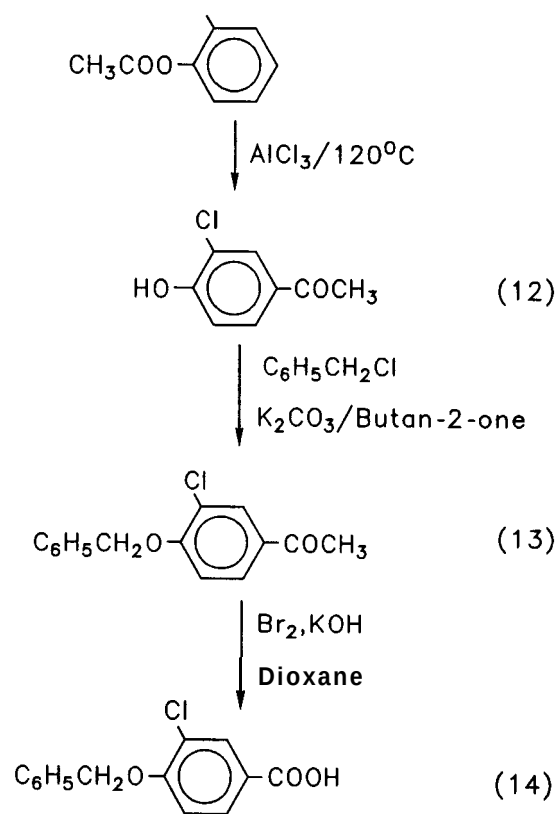


Fig.IIa.7

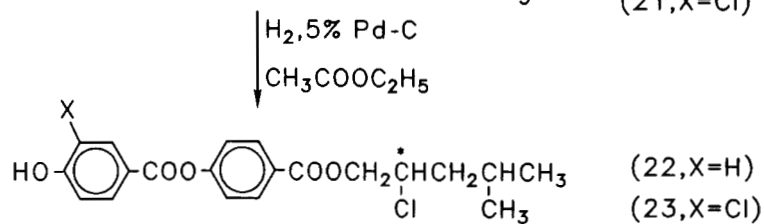
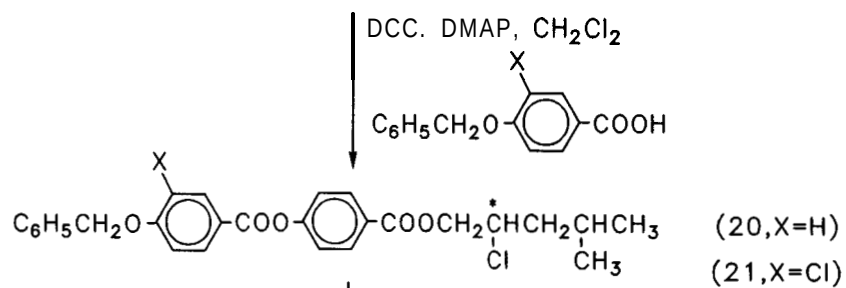
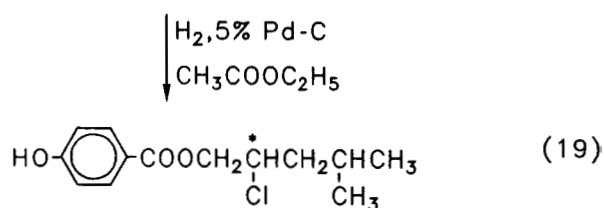
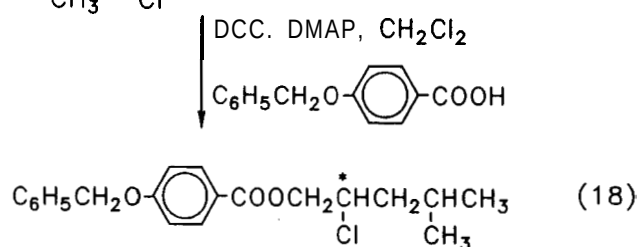
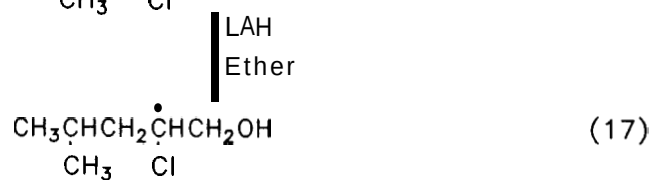
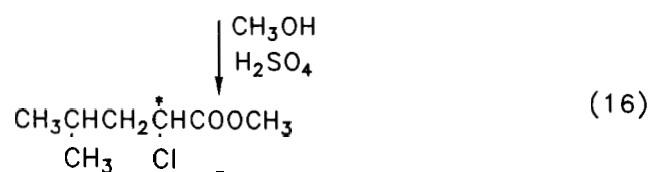
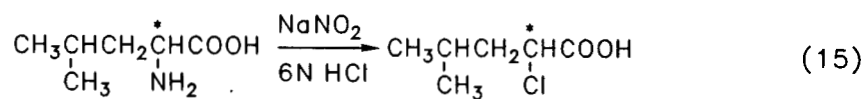


Fig.IIa.8

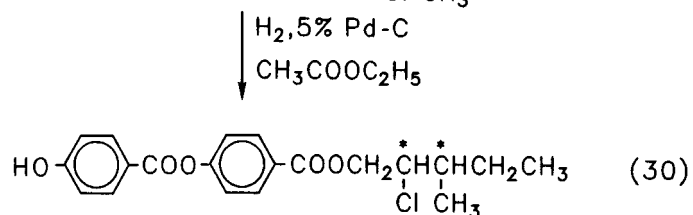
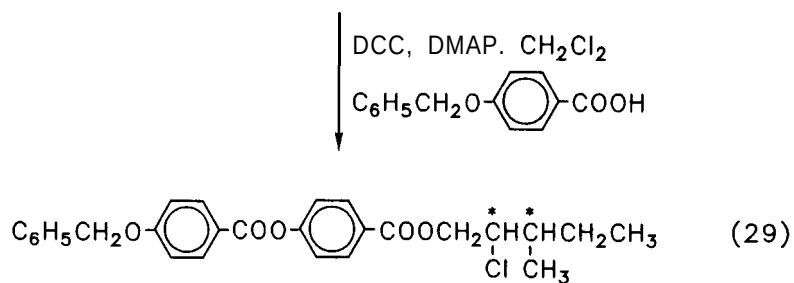
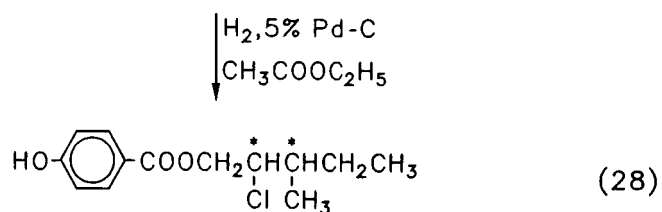
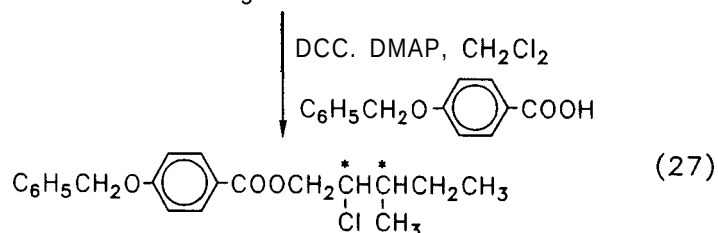
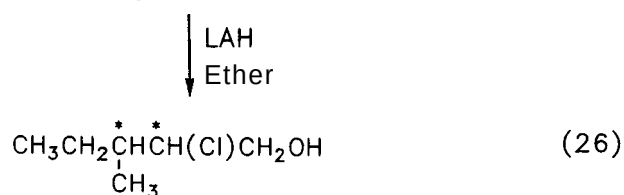
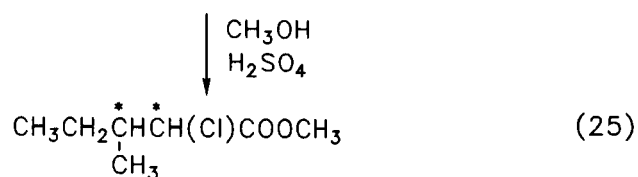
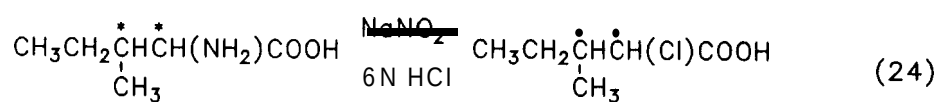


Fig.IIa.9

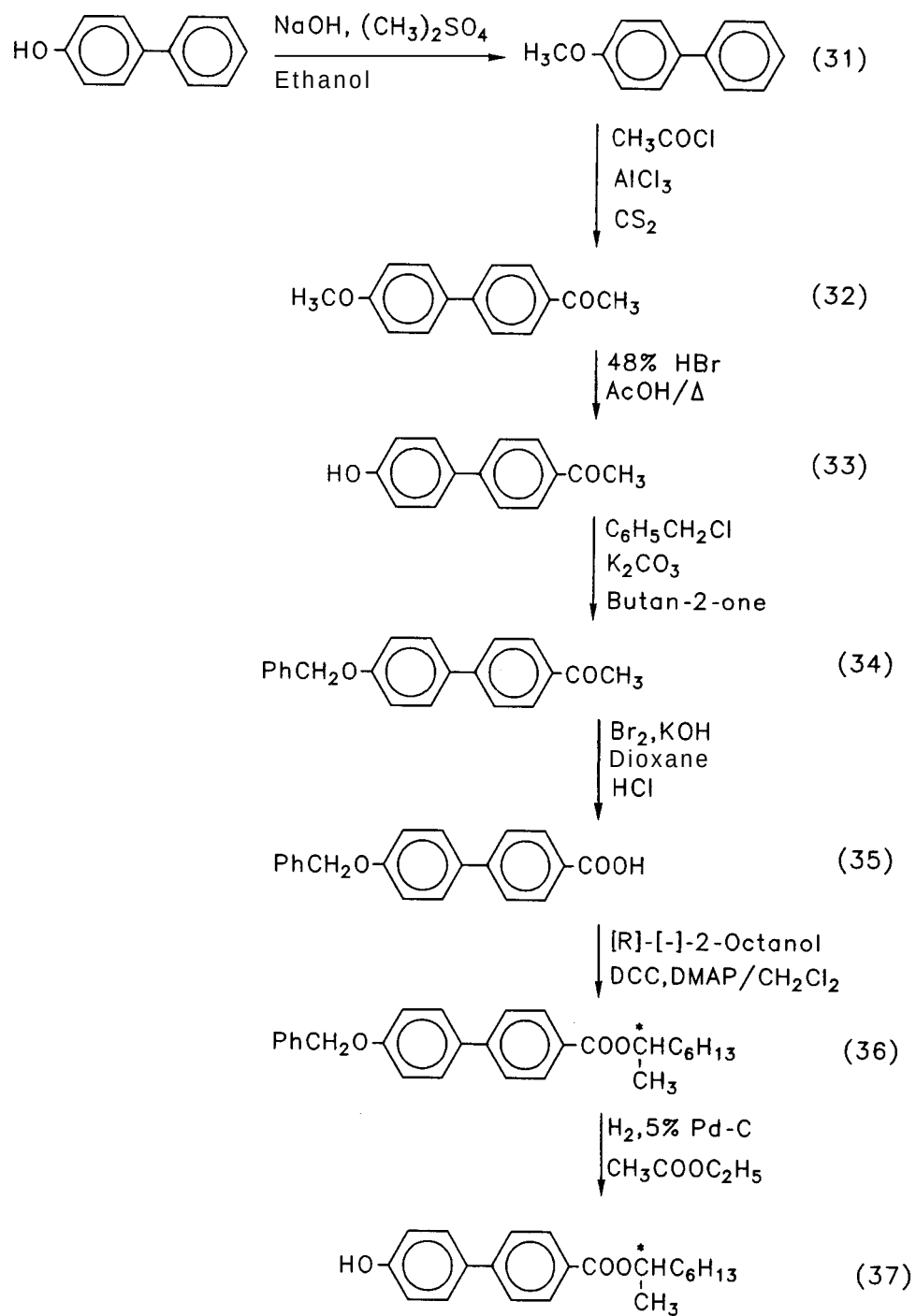


Fig.IIa.10

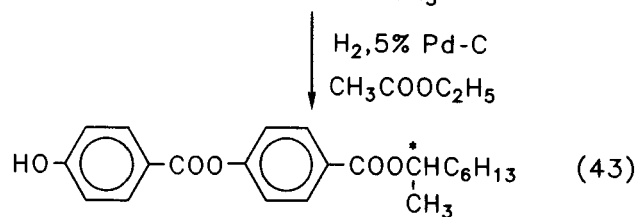
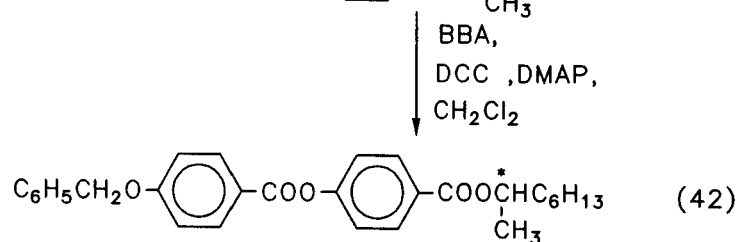
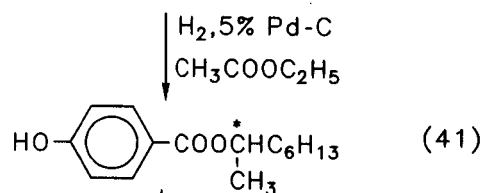
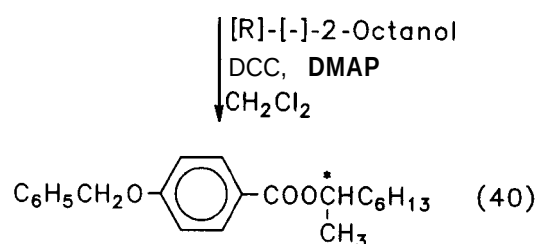
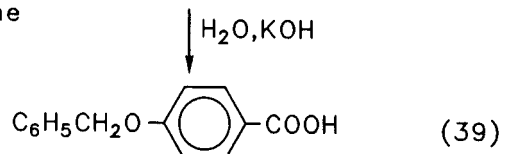
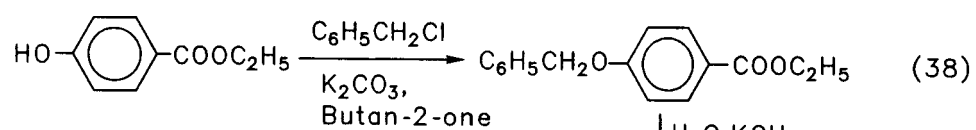


Fig.IIa.11

acetylchloride in the presence of pyridine. The resulting acetate, was then converted into the 3-chloro-4-hydroxyacetophenone, by Fries rearrangement using anhydrous aluminium chloride. The hydroxy compound was benzylated with benzylchloride in the presence of anhydrous potassium carbonate. Sodium hypobromite oxidation resulted in the formation of 3-chloro 4-benzyloxybenzoic acid.

The optically active chloro acids, *viz.* [S]-2-chloro-4-methylpentanoic acid and [2S, 3S]-2-chloro-3-methylpentanoic acid were obtained from I-leucine and I-isoleucine respectively, *via* their diazonium chloride solutions (Figs. 11a.8, 11a.9). The chloro acids were converted to their respective methyl esters by refluxing them in methanol in the presence of catalytic amount of concentrated sulphuric acid. The purified methyl esters were then reduced by lithium aluminium hydride to the corresponding alcohols. None of the reactions involved affected the absolute configuration of the chiral centres. The optically active alcohols were condensed with 4-benzyloxybenzoic acid. The products of these reactions were subjected to hydrogenolysis with 5% palladium on charcoal as the catalyst. The phenols obtained upon debenylation were reacted with ω -alkeneoxy naphthoic acids or with 4-benzyloxybenzoic or 3-chloro 4-benzyloxybenzoic acid in presence of N,N'-dicyclohexylcarbodiimide (DCC) and N,N'-dimethylaminopyridine (DMAP). The products obtained from the latter two cases were again subjected to hydrogenolysis with 5% palladium on charcoal as the catalyst. The phenols obtained upon debenylation were reacted with ω -alkeneoxynaphthoic acids in presence of dicyclohexylcarbodiimide and N,N'-dimethylaminopyridine.

The biphenyl portion of the target material was prepared starting from 4-methoxybiphenyl (Fig.11a.10). This compound was acetylated using anhydrous

aluminium chloride in carbondisulphide and then demethylated with aqueous 48% hydrobromic acid to give 4-hydroxy-4'-acetylbiphenyl, which was protected with benzylchloride as a benzylether. The 4-benzyloxy-4'-acetylbiphenyl was oxidised to the corresponding carboxylic acid using sodium hypobromite. This carboxylic acid was esterified with [R]-[-]-2-octanol in the presence of N,N'-dicyclohexylcarbodiimide and 4-N,N'-dimethylaminopyridine. The resulting ester was debenzylated by hydrogenolysis reaction using 5% Pd-C as catalyst.

The 4-benzyloxybenzoic acid was prepared by etherification reaction between benzylchloride and ethyl 4-hydroxybenzoate, followed by saponification and acidification. Its esterification with [R]-[-]-2-octanol was accomplished in the presence of a dehydrating agent such as N,N'-dicyclohexylcarbodiimide and 4-N,N'-dimethylaminopyridine as a catalyst as described earlier. Etherification reaction of 4-benzyloxyphenol with [R]-[-]-2-octanol was performed following a procedure described by Mitsunobu and Eguchi and inversion in absolute configuration was observed after the reaction (Fig.IIa.11). The deprotection of the phenolic group was achieved through a 5% palladium on charcoal catalysed hydrogenolysis reaction. The phenol was esterified with 4-benzyloxybenzoic acid and the same procedure was repeated in order to lengthen the molecule by another phenyl ring. The final compounds were obtained by a similar esterification reaction as shown in schemes Fig.IIa.12 to Fig.IIa.18. Experimental details of the reactions described above along with the relevant references are included in part III.

The transition temperatures were observed as a thin film by sandwiching the sample between a glass slide and a cover slip, under a polarising microscope equipped with a Mettler FP-80 heating stage. The enthalpies of transitions were determined from

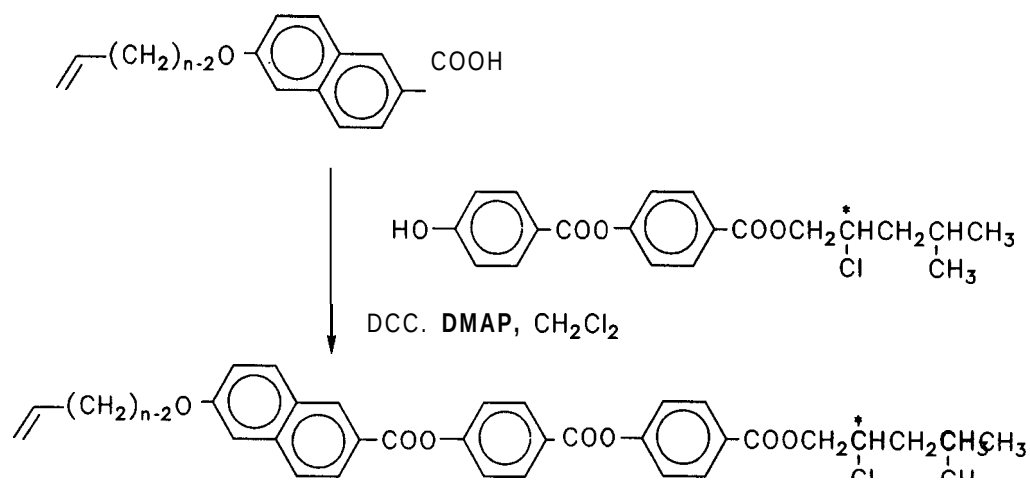


Fig.IIa.12

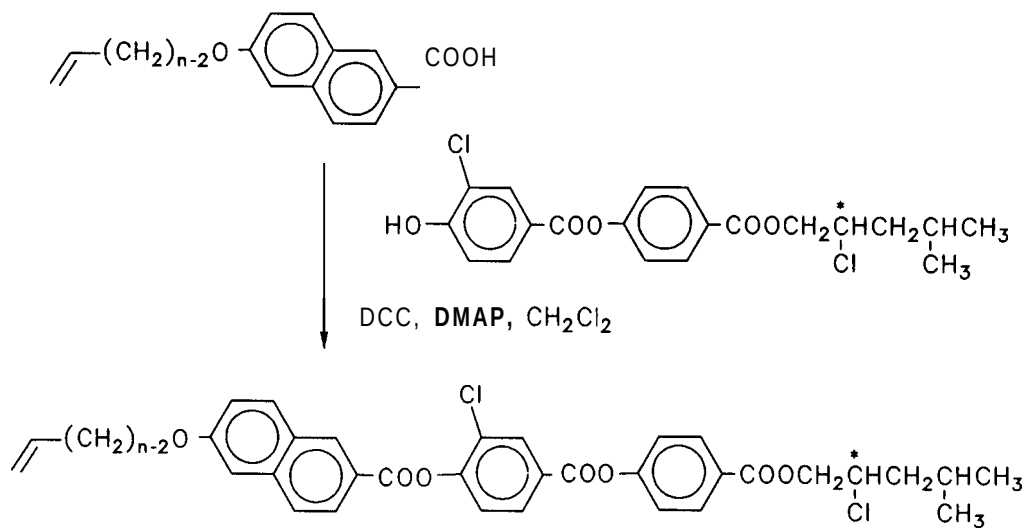


Fig.IIa.13

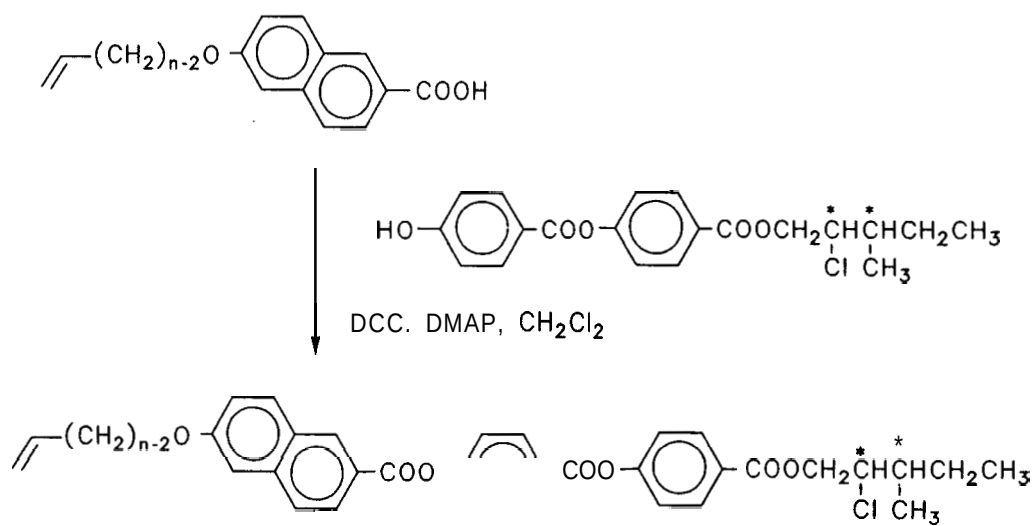


Fig.IIa.14

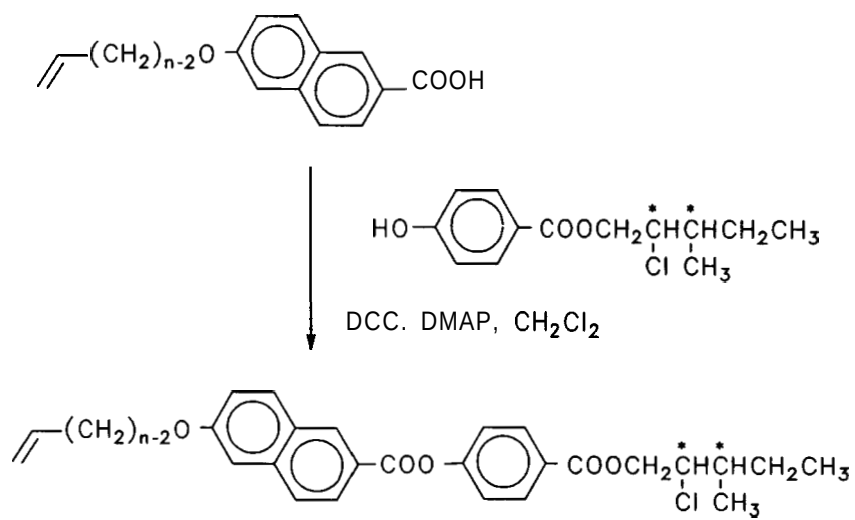


Fig.IIa.15

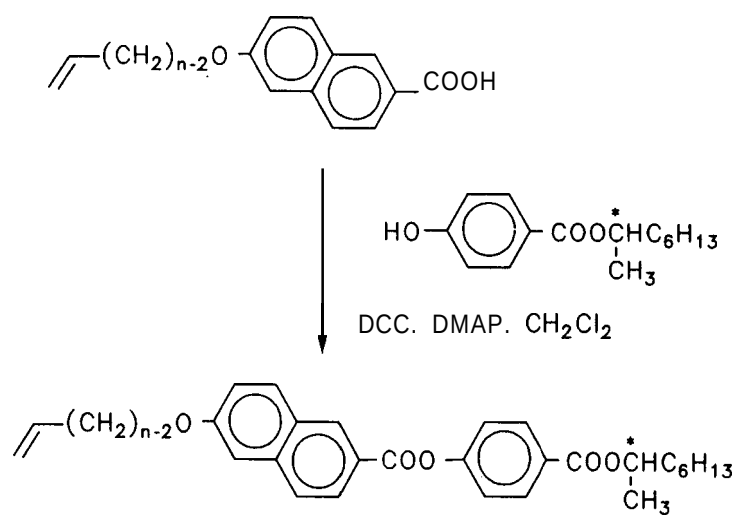


Fig.IIa.16

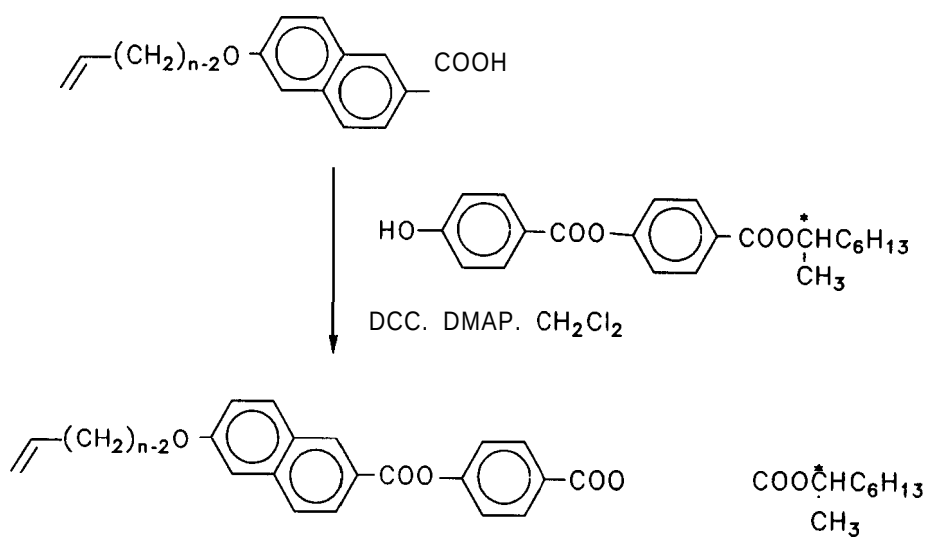


Fig.IIa.17

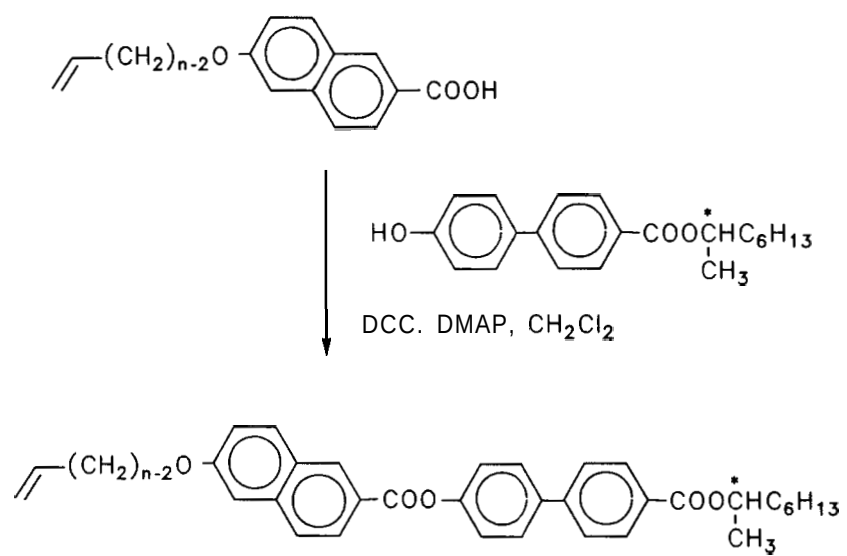


Fig.IIa.18

thermograms obtained on a Perkin-Elmer, Model DSC-4 or DSC-7 instrument for the monomers and Rheometric Scientific Differential Scanning Calorimeter for the polymers. The heating and cooling rates were 5.0 °C/min and 3.0 °C/min respectively for monomers and 10.0°C/min or 20.0°C/min for the polymers. The calorimeters were calibrated using pure indium as a standard. All experiments were conducted using samples sandwiched between ITO-coated glass plates. Mylar spacers were used to define the thickness of the cell (typically 5µm for the polarisation and tilt angle measurements). For spontaneous polarisation (P_s) measurements the triangular wave method was employed. To identify/confirm the presence of antiferroelectric and/or the "sub-phases" a low frequency (0.9 Hz) probing field had to be used. However, the measurements as a function of temperature were carried out at a higher frequency (10Hz) to avoid conductivity problems associated with low frequency large magnitude fields. The tilt angle (θ) of the molecules with respect to the smectic layer normal was calculated from the difference in the extinction positions of the sample between crossed polarisers under a near-DC (0.1 Hz) switching field. The field had to be high enough to unwind the helical structure.

The mesophases were observed as a thin film by sandwiching the sample between a glass slide and a cover slip. On cooling the isotropic liquid of monomer homologues N and A, the homeotropic and focal-conic texture of a S_A phase was observed. The S_{Ca}^* phase was hardly detectable by microscopic observation because its texture is similar to that of the S_A phase. The ferroelectric phase appears with a striated fan shaped or pseudo-homeotropic texture. As the temperature is decreased further, the antiferroelectric phase appears which looks like a ferroelectric phase only.

A planar alignment of the sample allowed to distinguish antiferroelectric phase from ferroelectric phase. It also reveals an intermediate phase $S_{C\alpha}^*$ between S_A (Plate IIa.1,2,3,4,5 and 6) and smectic C^* phases. In $S_{C\alpha}^*$ phase, the homogeneous coloured regions of the S_A phase becomes striated with thin, dark and clear bands parallel to the rubbing direction. At the transition to the smectic C^* phase, little perpendicular lines appear. The transition to the antiferroelectric phase was detected as a clear change of the texture. The new texture appears with large stripes growing perpendicular to the rubbing direction.

In the homologues of series K, R and I, the cholesteric phase appeared first from isotropic phase with a focal-conic or **Grandjean** plane texture. On further slow cooling, the transition N^*-S_A was observed via a helical TGB_A phase. The TGB_A phase existed for a very short temperature range ($\cong 0.1^\circ\text{C}$) and was identified as such by the observation of filament texture analogous to texture for TGB_A phase reported in literature. At lower temperature, the ferroelectric smectic C^* phase appeared both with broken fan shaped and plane textures in case of series I and K while in the case of series R no further change was observed.

IIa.2.1 Liquid crystalline properties of monomers

Naphthalene moiety has invoked attention because of some very interesting properties such as high optical birefringence in the nematic phase,⁵² formation of glassy states,⁵³ and quasi-bookshelf ferroelectric liquid crystalline order⁵⁴ in case of low molecular weight liquid crystals and important high performance polymeric fibers, *e.g.* VECTRATM, owe its properties to the 'crankshaft' geometry of this moiety.⁵⁵

Naphthalene moiety offers important structural properties such as molecular length and polarisability that positively influence the intermolecular interactions favouring the mesophase formation. Thus, the compact unit has been successfully used to promote the liquid crystal phases most suitable for display devices, *i.e.* nematic⁵⁶ or chiral smectic C phase.⁵⁷

Comparison of the mesomorphic properties of compounds containing a naphthalene moiety with other cores such as the phenyl or biphenyl systems has not been widely reported in literature.⁵⁸

Here we make an attempt to study the efficacy of the naphthalene moiety in yielding mesophases as compared to the other well known systems. A series of minor modifications were made on the parent structure R, shown in Fig.IIa.12, in an attempt to elucidate structure property correlation. The theme was to keep the naphthalene core unit untouched while modifying all other parameters in a stepwise fashion to study their effect.

It was reported by Goodby *et al.*,⁵⁹ that the naphthalene moiety if present at one end of the core promotes the formation of a smectic A phase; and if it is present as a central ring system of the core *i.e.* joined by another aromatic system at least on one side promotes the formation of the smectic C phase. There it was argued that when the naphthalene moiety is in the central position of the core it produces an overall zig-zag shape that is conducive to the formation tilted phase, but when it is in a terminal position within the core its structure tends to bend or kink the core out of line. Effectively, the breadth of the naphthalene ring in the terminal position is being experienced more in interactions with neighbouring molecules than it would if it were in a central position. This has been illustrated by the following figure (Fig IIa.19).

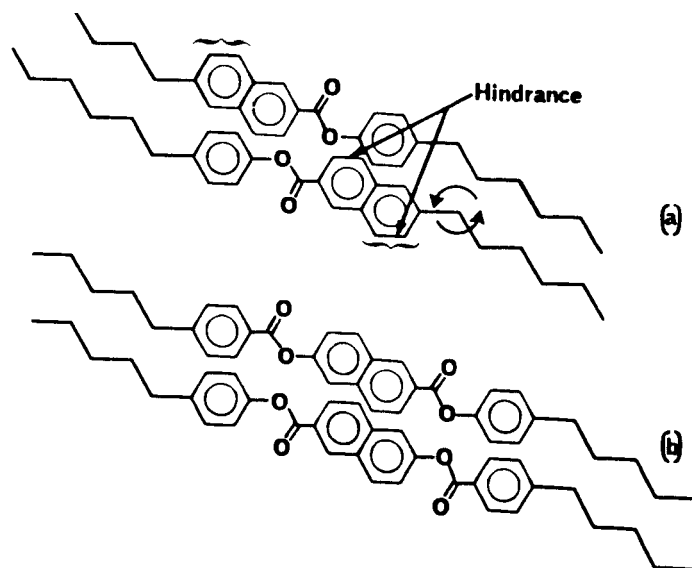


Fig.IIa.19

We report here several series of compounds that contain naphthalene unit as a terminal unit of the core. All, except the lower homologues, show a chiral smectic C phase. Some of these also show the novel antiferroelectric phase as well. It is interesting to note that the antiferroelectric phase seems to get stabilised, displaying a fairly wide temperature range as compared to the corresponding phenyl unit containing core.⁶⁰ It is also worthwhile to note that none of these novel compounds display the ferrielectric phase.

We propose the following model to argue how the ferroelectric phase gets stabilised in the compounds that we report here. **All** the compounds synthesised have a terminal alkene group. It is felt that this terminal alkene plays an important role. The π -electrons of the double bond has its own polarisability which tend to stabilise the antiferro like configuration of molecules. Thus, it aids in tilting of the molecules in alternate layers stabilising first the ferroelectric phase then the antiferroelectric phase. This may also be a reason why there is a total elimination of the ferrielectric phase, which in the normal circumstances would have been expected to exist between the ferroelectric and antiferroelectric phase as in the case of analogous biphenyl substituted cores. This implies a strong interaction between the alternating layers in the smectic phase structure. It can still be observed that, as per **Goodby's** argument, delocalised electrons of the core would stabilise the smectic A phase. The temperature range of the smectic A phase is very wide in almost all the compounds synthesised.

Unusual stabilisation of the antiferroelectric phase has also been reported by Wu *et al.*⁶¹ in some naphthalene compounds. In those cases the naphthalene moiety was at terminal end of the core close to the chiral center *viz.* the chiral group was directly attached to the core of the molecule. Interestingly their core structure was the

reverse of the ones reported for one of the series, A, here. Though, direct comparison of results would be inappropriate, it is significant to note that the P_s values and the tilt angle measured by us is higher for compounds of similar terminal chain length.

The tables (Tabs.IIa.1-4) reveal that the parent R series compounds do not show a chiral smectic C phase. Infact, these show less ordered cholesteric phase. Varying the core by introduction of a chloro group in the central ring (the K series), reveals a very short temperature range of TGB_A phase. The identification of this phase was done by observation of textures and comparing with analogous ones reported in literature. It is a small but structurally important fact that a TGB_A phase was observed in a compound that shows predominantly smectic A phase. It is well known, as noted earlier, that for the formation of TGB phase strong fluctuations from the cholesteric or the blue phase should penetrate the lower lying smectic phase. Also, the smectic phase should be of small temperature range so that it can easily be disturbed by the penetrating fluctuations from the cholesteric phase. Both these factors contribute to stabilise the TGB phase. Here, in the K series, the smectic phase has a fairly long temperature range. Thus, it is possible that the fluctuations induced by the cholesteric phase in this compound is very strong.

The I series of compounds show the smectic C* phase. The only difference between the I series and the parent R series is in the chiral centre. R series has 2-chloro 4-methylpentyl unit while the I series has 2-chloro 3-methylpentyl unit. Effectively, a methyl group has been moved one carbon atom closer to the core of the molecule in case of the I series as compared to the R series. This, perhaps, causes an increase in the effective chain length and enables the formation of a tilted smectic phase. Conversely, the protruding methyl group in the case of R series increases the overall breadth of the

Tab.IIa.1 : Transition temperatures (°C) and enthalpies (Jg⁻¹) of monomers.

Monomers	n	K	S _A		TGB _A		Ch	BP		I		
R-4	4	●	104.80	●	210.60	-	210.70'	●	212.60	-	213.20'	●
			50.80		7.93				0.85			
R-8	8	●	95.80	●	199.50	—		-	200.50	-	201.10'	-
			51.91		7.42				0.98			
R-9	9	●	88.50	●	197.00	—		-	201.50	-	202.00'	-
			57.65		5.43				1.34			
K-4	4	●	77.10	●	133.60	●	133.70'	●	167.70	-	168.20'	●
			55.23		8.74				1.03			
K-8	8	●	65.50	●	149.10	—		-	159.70	-	161.20'	●
			52.45		5.64				1.45			
K-9	9	●	63.80	●	148.20	—		-	158.30	-	158.60'	●
			66.88		6.45				1.22			

- The enthalpy for the transition could not be measured.

Tab.IIa.2 : Transition temperatures (°C) and enthalpies (Jg⁻¹) of monomers.

Monomers	E	K	S _C *	S _A	Ch	I
I-4	1	•	116.80	•	213.00	•
			56.76		5.33	1.33
I-8	8	•	98.40	•	144.70	•
			55.65	0.12		5.91
I-9	9	•	98.10	•	148.00	•
			58.13	0.09		6.08

Tab.IIa.3 : Transition temperatures (°C) and enthalpies (Jg⁻¹) of monomers.

Monomer	n	K	S_A		I	
S-4	4	•	(79.20)	•	80.70 25.74	•
S-8	8	•	78.00 34.48	•	85.20 8.32	•
S-9	9	•	70.70 29.27	•	88.20 7.75	•
H-4	4	-		—	45.20 27.25	•
H-8	8	•	(40.05)	•	60.05 5.22	-
H-9	9	•	(43.10)	•	61.20 4.96	•

Tab.IIa.4: Transition temperatures (°C) and enthalpies (Jg⁻¹) of monomers.

Monomer	n	K	$S_{C_A}^*$	Sc^*	$S_{C_\alpha}^*$	S_A	I
N-4	4	-	118.20 27.22	-	(101.00) 0.03	199.30 0.10	200.00 5.12
N-8	8	•	97.40 28.14	• 0.03	119.20 0.02	132.20 0.07	132.70 7.50
N-9	9	•	91.20 29.30	• 0.05	139.10 0.03	143.20 0.07	175.90 6.90
A-4	4	-	128.30 33.25	-	-	-	183.90 8.27
A-8	8	•	92.50 30.77	• 0.04	101.30 0.02	123.30 0.09	125.50 7.93
A-9	9	-	80.80 30.10	• 0.06	102.80 0.05	127.40 0.06	132.70 7.90

molecule and the resulting steric interactions stabilises the smectic A phase over the tilted smectic phase. Such observations have been made earlier in the literature.⁶²

It can also be seen from Tabs IIa.1-4 that if the core length is reduced then the tilted smectic phase vanishes completely. As can be seen in the case of H series, even the smectic A phase becomes monotropic for example compound H-4, and exists enantiotropically over a small temperature range in the higher homologues. The compound of series S show a higher thermal stability when compared series H, though both have only three ring systems in the core. The difference lies in the chiral moiety. The S series has 3-chloro 4-methylpentyl unit while the H series has a 1-methylheptyl unit. It is not clear as to why the stabilisation of the smectic phase occurs, although an indication can be gathered from the fact that the chloro group present in the chiral centre of the S series would induce a lateral dipole, which could in principle stabilise the smectic ordering.

The remaining two series of compounds, series N and A, are quite interesting. Higher homologues of both these series show a sequence of $S_A - S_{C\alpha}^* - S_{C^*} - S_{C_A}^* - K$. The effective stabilisation of the tilted smectic phases over the smectic A phase by the terminal alkene has already been discussed earlier.

Both the series show lower thermal stability compared to the other four ring (considering the naphthalene unit as two rings) series synthesised. This enabled the measurement of spontaneous polarisation and tilt angle easy. It can be seen from Fig.IIa.20 that the N series has a higher polarisation value and tilt compared to the A series. In both the cases the polarisation saturates at about 85nC/cm^2 . The maximum observed was for compound N-8 = 90nC/cm^2 . A look at the temperature dependent optical tilt angle measurements show that the tilt saturates at about 22° . This holds

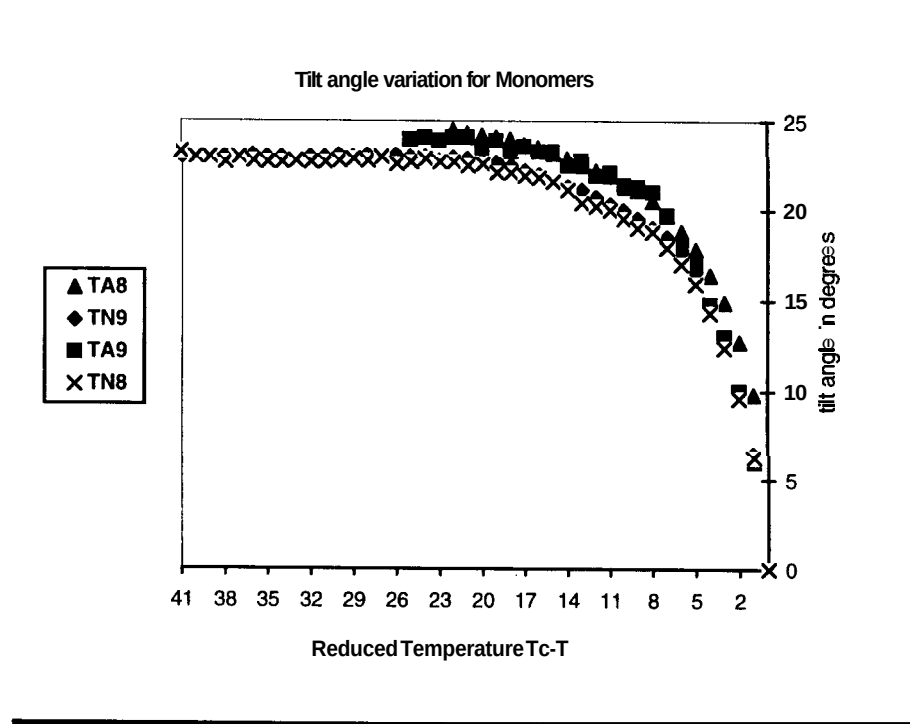
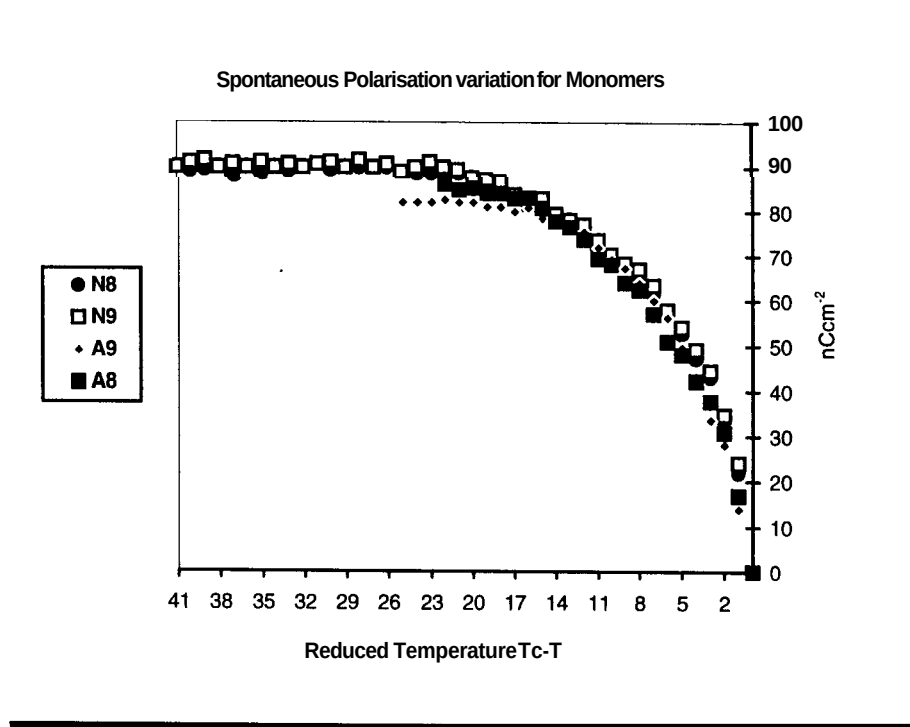


Fig.IIa.20

good for both series **A** and **N**. The maximum tilt was observed for compound **N-8**, 24° . Thus, there is not much difference in the value of polarisation or the tilt angle between the two series of compounds though structurally one ester group has been eliminated from the core of the **A** series. It can therefore be implied that the role played by the central ester group is minimal in determining the polarisation or optical tilt angle of this compound. This is because the particular ester group is deeply embedded into the core of the molecule and its steric and dipolar contribution is effectively cancelled by steric averaging due to fast rotation of the molecule around its long axis.

IIa.3 Physical measurements

IIa.3.1 Spontaneous polarisation

The magnitude of spontaneous polarisation, P_s , is of fundamental importance in the study of ferroelectric liquid crystal (FLC) devices.^{63,64} In order to synthesise a ferroelectric liquid crystal with large P_s thereby achieving lower operating voltages, it is essential to know the relationship between magnitude of P_s and molecular structure.⁶⁵ The interplay between molecular structure and the magnitude of P_s is not yet clear (symmetry considerations do not give any information regarding the magnitude of P_s ; it only predicts the existence of ferroelectricity in liquid crystals) and only general rules can be discussed, although many studies have been made.⁶⁶ The following factors seem to play an important role in determining the magnitude of P_s .

1. The size and nature of the lateral dipole at the chiral centre.⁶⁷
2. The degree to which the rotations of the molecules especially the chiral centre are hindered.⁶⁸

3. The degree of coupling between the dipole at the chiral centre with any other dipoles in the molecule.⁶⁹
4. The distance between the chiral centre and the central rigid core.⁷⁰
5. The alky chain length.⁷¹

In addition, for the side chain ferroelectric polymers:

6. The extent of decoupling of the side chain from the main chain.
7. The rotational viscosity of the polymer in its liquid crystalline state.

Even though several studies have been carried out to confirm the above empirical observations, concrete links between the molecular structure and the physical properties have still not been established, especially on the effect of polymerisation on electro-optic properties. Towards this, in the present investigations, a few selected monomers and polymers were examined so that relation between molecular structure and property, including the effect of polymerisation on the magnitude of polarisation could be understood better.

The following sections describe, in detail, the experimental set-up including the apparatus used to measure P_s , the techniques employed for aligning the sample and the method of data acquisition and analysis, followed by the results obtained for the monomers and the polymers.

IIa.3.1.1 Measurement of spontaneous polarisation (P_s)

Several methods employed for the measurement of P_s in solid ferroelectrics, have been used in the case of FLCs also.⁷² In addition, a few techniques have been developed specifically for liquid crystals.⁷³ Among these a successful and very versatile method is the triangular wave method.⁷⁴ Another popular method to measure the

spontaneous polarisation directly is the field reversal method, wherein, the induced current is measured by rapidly reversing the applied field. But difficulties arise from the large conductive and capacitive current which are comparable to the current arising due to the polarisation realignment. It is not easy to draw the base line unambiguously because of the contribution of these unwanted currents, and hence it is difficult to measure polarisation accurately.⁶⁷ The principle and advantages of using triangular wave method are described below.

Liquid crystals (including polymeric liquid crystals, PLCs), are not good insulators. The presence of ionic impurities make them fairly conductive. PLCs can also act as dielectrics when they are filled in a cell of the type described above. Thus, such a cell can be regarded as a resistor (R) and a capacitor (C) connected in parallel. The current $I(t)$ induced in a ferroelectric liquid crystal cell by applying a field $V(t)$ is written as a sum of the following three contributions :

- the first due to the charge accumulation to the capacitor I_c ,
- the second due to the polarisation realignment I_p , and
- the third due to the ion flow I_i .

Thus, we obtain,

$$I = I_c + I_p + I_i = C \frac{dV}{dt} + \frac{dP}{dt} + \frac{V}{R}$$

where P is the amount of charge induced per unit area by the polarisation realignment.

The following diagram (Fig. IIa.21) shows the current induced by rapidly reversing a field (a) and by applying a field with a triangular form (b). Here, three contributions, I_c , I_p and I_i and the overall profiles of the induced current expected are

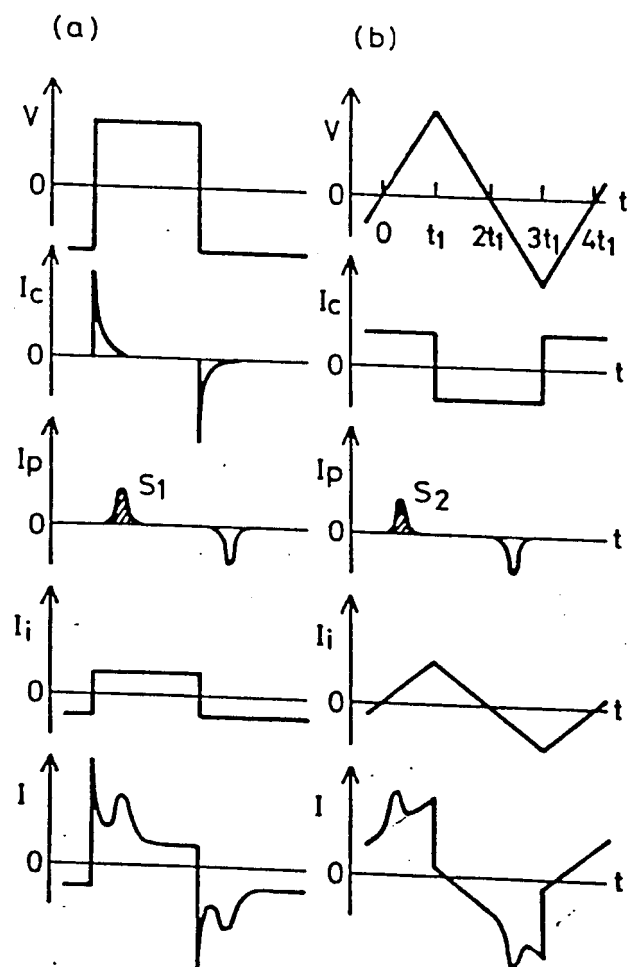


Fig.IIa.20

shown for each case. In case (b), it is assumed that the helix remains unwound between $t_1 < t < 2t_1$ and the reversal of the polarisation is completed between $2t_1 < t < 3t_1$. Therefore, the area S_2 is twice the spontaneous polarisation, and should be identical to the area S_1 in case (a). The difference between the two cases prominently appears in the base-line to separate the contribution I_c from the overall signal I . When a rapidly reversing field is applied, the voltage remains constant between the interval $2t_1 < t < 3t_1$, and hence the current varies. This current contributes to the peak observed for polarisation reversal current in a complicated fashion. Hence, it is difficult to separate the capacitive contribution. Whereas, when a triangular wave is applied, the net capacitive effect is shifting of baseline, which brings about the advantages of the triangular wave method. This is especially important when the operating frequencies are low. Hence, the triangular wave method becomes the method of choice when polymers are subjected to polarisation studies (where the response times are large).

IIa.3.2 X-ray studies

The mode of packing of molecules and the types of order present in a mesophase are revealed by X-ray diffraction studies. The well-known Debye Scherrer technique was used for powder samples. It does not provide information regarding spatial orientation but gives all the reticular spacings which are usually sufficient to distinguish between broad classes of liquid crystalline phases. For complete characterisation however, well-oriented samples are required.^{75,76} Orientation of sample in capillaries could be achieved by application of strong magnetic field across the isotropic-nematic or isotropic-smectic phase transition. An alternative procedure

was to draw a fiber of polymer sample from out of the mesophase and quenching the LC array in the glassy state so that it could be examined at room temperature.

Ila.3.2.1 Powder samples

The diffraction pattern of a powder sample can be divided into inner rings at small angles, and outer rings at large angles. Small diffraction angles are of the order of 3° and correspond to distances of about 30 angstroms. The large diffraction angles are of the order of 20° and corresponds to distances of about $4.5\text{\AA}$ for the usual wavelengths ($\text{CuK}\alpha = 1.54\text{\AA}$). The inner rings are indicative of longer layer spacings while the outer rings correspond to short preferred spacings occurring in the lateral packing arrangement of the molecules. The appearance of a broad halo or a sharp ring indicates the degree of order qualitatively.

Ila.3.2.2 Oriented samples

The marked anisotropy of the molecular organisation in oriented nematic samples is shown by two symmetrical wide angle crescents arising from spectral correlation between mesogenic units. In the case of oriented smectics the patterns are much like those of nematics but they are more intense and with a less pronounced arc. Strong sharp reflections seen at small angles show the extensive layer-like correlations.

X-ray diffraction can be used to determine the tilt angle of the molecules in ferroelectric phases.⁷⁷ But the tilt obtained here is average tilt of the whole molecule and not just the core of the molecule. This is defined as the steric tilt angle. The optic and steric angles usually differ because the molecules are not linear in shape. The steric tilt angle is determined by the expression

$$\cos\theta = d/l$$

where θ is the steric angle, d is the lamellar spacing measured by X-ray and l is the length of the molecule. The length of the molecule for a compound showing S_A - S_C^* phase transition is assumed to be equal to the lamellar spacing at the S_A - S_C^* phase transition.

Ila.3.3 Optical tilt angle

It is difficult to define the optical tilt angle in ferroelectric mesophases because it depends on the position of a reference coordinate system. Assuming the normal to the layer plane to be one of the reference directions, the angle between the optic axis of an ensemble of molecules and this axis is termed the optical tilt angle. For most materials the optic axis is determined by the relative positions of the core of the molecules and strongly dipolar functionalities that effectively determine the axis. Thus the optic axis can be used to investigate the inclinations of the cores relative to the layer planes of the phase.

The optical tilt angle can be determined in ferroelectric liquid crystals by electrical studies. The ferroelectric phase is poled by a strong DC field so that the material aligns in a single direction. The cell is placed on a microscope stage and oriented under crossed polarisers of a microscope such that extinction is obtained. The polarity of the applied DC field is then reversed and the field of view becomes lighter as the molecules are reoriented through an angle equal to twice the tilt angle. The cell on the microscope stage is rotated in order to bring the field of view back to extinction. This angle of rotation is divided by two to give the optical tilt angle. The temperature dependence of this optical tilt angle can be determined by placing the cell inside an oven whose temperature can be controlled accurately.⁷⁸

The tilt angle obtained both from optical and X-ray diffraction patterns, can be used as a probe to study the internal structure of the tilted phases. The results indicate the location of the cores of the molecules, how their position change with temperature and how they are affected by the structural changes.

References

- 1 N. A. Clark and S. T. Lagerwall, *Ferroelectric Liquid Crystals: Principles, Properties and Applications*, **ed. Goodby et al.**, Gordon and Breach Science Publishers, (1991).
- 2 R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. de Phys.*, **36**, L69 (1975).
- 3 S. Garoff and R. B. Meyer, *Phys. Rev. Lett.*, 38, 848 (1977).
- 4 S. Garoff and R. B. Meyer, *Phys. Rev. A*, 19, 388 (1979).
- 5 A.D.L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe and A. Fukuda, *J. Appl. Phys.*, 27, L729 (1988).
- 6 A.D.L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.*, 29, L131 (1989).
- 7 A. M. Levelut, C. Germain, P. Keller, L. Liebert and J. Billard, *J. Phys. (Paris)*, 44, 623 (1983).
- 8 A. Fukuda, Y. Takanishi, T. Ishikawa and H. Takezoe, *J. Mater. Chem.*, 4, 997 (1994).
- 9 V. Laux, N. Isaert, H. T. Nguyen, P. Cluzeau and C. Destrade, *Ferroelectrics*, 179, 25 (1996).
- 10 G. W. Gray, in "Liquid Crystals and Plastic Crystals", **Vol.1, eds. G.W. Gray and P.A. Winsor**, Ellis Horwood, Chichester, England, 1974; G.W. Gray, in "Advances in liquid Crystals", **Vol.2, ed. G. H. Brown**, Academic Press, New York, 1976.
- 11 G.W. Gray, "Molecular structure and the Properties of Liquid Crystals", Academic Press, London and New York, (1962).

- 12 K. Mohr, S. Kohler, K. Worm, G. Pelzl, S. Diele, H. Zschke, D. Demus, G. Andersson, I. Dahl, S.T. Lagerwall, K. Skarp and B. Stebler, *Mol. Cryst. Liq. Cryst.*, 146, 151 (1987); N.H. Tinh, C. Salleneuve, A. Babeau, J.M. Galvan and C. Destrade, *Mol. Cryst. Liq. Cryst.*, 151, 147 (1987); N.H. Tinh, A. Babeau and C. Destrade, *Mol. Cryst. Liq. Cryst. (Lett.)*, 4, 87 (1987); B. Otterholm, *Mol. Cryst. Liq. Cryst.*, 146, 189 (1987); J. W. Goodby and T. M. Leslie, *Liquid Crystals and ordered Fluids*, **Vol. 4**, eds. A. C. Griffin and J. F. Johnson, Plenum Press, New York, London, 1984, p.1; S.M. Kelly, R. Buchecker and M. Schadt, *Liq. Cryst.*, 3, 1125 (1988); S.M. Kelly and A. Villiger, *ibid.*, 3, 1173 (1988); A.M. Lackner, S.M. Wong, K.S. Lim, J.D. Margerum and M.E. Neubert, *Liq. Cryst.*, 5, 1259 (1989); J. Nakauchi, Y. Kageyama, S. Hayashi and K. Mori, *Liq. Cryst.*, 62, 1011 (1989); S. H. Takenaka, T. Ikemoto and S.H. Kusabayashi, *J. Chem. Soc. Chem. Commz.*, 1221 (1986).
- 13 Y. Suzuki, T. Hagiwara, I. Kawamura, N. Okamura, T. Kitazuma, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe and A. Fukuda, *Liq. Cryst.*, **6**, 167 (1989).
- 14 E. P. Janulis Jr., J.C. Novack, G.A. Pappolymerou, M. Tristani-Kendra and W.A. Huffman, *Ferroelectrics.*, 85, 375 (1988).
- 15 S. M. Kelly, R. Buchecker, H. Fromm, Jr., and M. Schadt, *Ferroelectrics*, 85, 385 (1988).
- 16 K. Yoshino, M. Ozaki, S.H. Kishio, T. Sakura, N. Mikami, R. Higuchi and M. Honma, *Mol. Cryst. Liq. Cryst.*, 144, 87 (1987).
- 17 T. Uemoto, K. Yoshino and Y. Inuishi, *Jpn. J. Appl. Phys.*, 18, 1261 (1979).
- 18 T. Geelhaar, *Ferroelectrics*, 85, 329 (1988).
- 19 T. Sakurai, N. Mikami, R. Higuchi, M. Honma and K. Yoshino, *Ferroelectrics.*,

- 85,469 (1988).
- 20 K. Furukawa, K. Terashima, M. Ichihashi, S. Saitoh, K. Miyazawa and T. Inukai, *Ferroelectrics*, **85**, 451 (1988).
- 21 T. Kitamura, A. Mukoh, M. Isogai, T. Inukai, K. Furukawa and K. Terashima, *Mol. Cryst. Liq. Cryst.*, **136**, 167 (1986).
- 22 J. W. Goodby, I. Nishiyama, A. J. Slaney, C. S. Booth and K. J. Toyne, *Liq. Cryst.*, **14**, 37 (1993).
- 23 J. S. Patel and J.W. Goodby, *Mol. Cryst. Liq. Cryst.*, 144, 117 (1987).
- 24 S. M. Kelly, R. Buchecker, H. Fromm, Jr., and M. Schadt, *Ferroelectrics*, 85, 385 (1988).
- 25 H. Taniguchi, M. Ozaki, K. Nakao, K. Yoshino, N. Yamasaki and K. Satoh, *Jpn. J. Appl. Phys.*, 27,452 (1988); B. Shivkumar, *Ph.D* thesis, Bangalore University, Bangalore, 1991.
- 26 B. Shivkumar, *Ph.D* thesis, Bangalore University, Bangalore, 1991.
- 27 M. Marcos, J.L. Serrano, M.T. Sierra, J. Etxebarria and A. Ezcurra, *Ferroelectrics*, **85**, 415 (1988)
- 28 G. Durand and P. H. Martinot-Lagarde, *Ferroelectrics*, 24, 89 (1980).
- 29 J. Barbera, E. Melendez, J.L. Serrano and M.T. Sierra, *Ferroelectrics*, 85,405 (1988).
- 30 G. W. Gray and B. Jones, *J. Chem. Soc*, 236 (1955).
- 31 S. Kobayashi, S. Ishibashi and S. Tsuru, *Mol. Cryst. Liq. Cryst. (Lett.)*, **7**, 105 (1990).
- 32 B. Otterholm, M. Nilsson, S.T. Lagerwall and K. Skarp, *Liq. Cryst.*, 2,757

- (1987).
- 33 T. Sakurai, N. Mikami, M. Ozaki and K. Yoshino, *J. Chem. Phys.*, 85,585 (1986).
 - 34 S. Kobayashi and S. Ishibashi, *Mol. Cryst. Liq. Cryst. (Lett)*., 7, 53 (1990).
 - 35 G. W. Gray, in "*Molecular Chemistry for Electronics*", *Proc. Roy. Soc. Disc.* (1989); G. W. Gray and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 37, 157 (1976); G. W. Gray, C. Hoggs and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **75**, 95 (1981); L. K. M. Chan, G. W. Gray, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **158B**, 209 (1988).
 - 36 M. Chambers, R. Clemitson, D. Coates, S. Greenfield, **J.A. Jenner** and I. Sage, *Liq. Cryst.*, 5, 153 (1989).
 - 37 P. Keller, L. Liebert and S. Strzelecki, *J. Phys. (Paris)*, 37, 3 (1976).
 - 38 D. M. Walba, R. T. Vohra, N. A. Clark, M. Handschy, J. Xue, D. S. Parmar, S. T Lagerwall and K. Skarp, *J. Am. Chem. Soc.*, 108,7424 (1986).
 - 39 W. Kuczynski, S. Lagerwall, M. Matuszczyk, K. Skarp, B. Stebler and D. M. Walba, *Mol. Cryst. Liq. Cryst.*, 146, 173 (1987).
 - 40 M. Murakami, S. Miyake, T. Masumi, T. Ando, F. Fukami, T. Takashashi, K. Setoh and T. Tahara, *Mol. Cryst. Liq. Cryst.*, 162, 149 (1988).
 - 41 P. Keller, *Mol. Cryst. Liq. Cryst.*, 102,295 (1984).
 - 42 J. W. Goodby, *Science*, 231, 350 (1986).
 - 43 P. H. Martinot-Lagarde, R. Duke and G. Durand, *Mol. Cryst. Liq. Cryst.*, 75, 249 (1981)
 - 44 J. W. Goodby, J.S. Patel and E. Chin, *J. Phys. Chem.*, **91**, 5151 (1987).
 - 45 K. Yoshino, M. Ozaki, K. Nakao, H. Taniguchi, M. Yamasaki and K. Satoh, *Liq.*

- Cryst.*, 5, 1203 (1989); K. Yoshino, K. Nakao, M. Ozaki, R. Higuchi, N. Mikami and T. Sakurai, *ibid.*, 5, 1213 (1989).
- 46 T. Geelhaar, H.A. Kurmeier and A.E.F. Wachtler, *Liq. Cryst.*, 5, 1269 (1989).
- 47 A. Yoshizawa, H. Kikuzaki, T. Hirai and M. Yamane, *Jpn. J. Appl. Phys.*, 28, L-1988 (1989).
- 48 L. Pasteur, *Ann. Chim. et Phys.* [3] 24,442 (1848).
- 49 J. Billard, *J. de Phys.*, 46, 1241 (1985).
- 50 J. W. Goodby and E. Chin, *Liq. Cryst.*, 3, 1245 (1988).
- 51 O. Mitsunobu and M. Eguchi, *Bull. Chem. Soc. Jpn.*, 44,3427 (1971).
- 52 M. Hird, K. J. Toyne, G. W. Gray, S. E. Day and D. G. McDonnel, *Liq. Cryst.*, 15, 123 (1993).
- 53 W. Welder, D. Demus, H. Zashke, K. Mohr, K. W. Schafer and W. Weissflog, *J. Mater. Chem.*, 1, 347 (1991).
- 54 A. Mochizuki, K. Motoyoshi and M. Nakatsuka, *Ferroelectrics*, 122, 37 (1991).
- 55 G. Calundann, M. Jaffe, R. S. Jones and H. Hoon, *Fiber Reinforcements for Composite Materials*, ed. A. R. Bunsell, (Amsterdam), p 211.
- 56 T. Sierra, J. L. Serrano, M. B. Ros, A. Ezcurra and J. Zubia, *J. Am. Chem. Soc.*, 114,7645 (1992).
- 60 M. Hird, K. J. Toyne, G. W. Gray, S. E. Day and D. G. McDonnel, *Liq. Cryst.*, 15, 123 (1993).
- 58 Y. Gonzalez, M. B. Ros, J.L. Serrano and M.A.Perez-Jubindo, *Liq. Cryst.*, 18,751 (1995); J. W. Goodby, *Ferroelectric Liquid Crystals: Principles, Properties and Applications*, ed. J. W. Goodby et al., Gordon and Breach Science Publications, 1991.

- 59 J. W. Goodby, *Ferroelectric Liquid Crystals: Principles, Properties and Applications*, **ed.** J. W. Goodby et al., Gordon and Breach Science Publications, 1991.
- 60 V. Faye, J. C. Rouillon, C. Destrade and H. T. Nguyen, *Liq. Cryst.*, **19**, 47 (1995).
- 61 S. L. Wu, D. G. Chen, S. J. Chen, C. Y. Wang, J. T. Shy and G. H. Hsiue, *Mol. Cryst. Liq. Cryst.*, 264, 39 (1995).
- 62 Y. Gonzalez, M. B. Ros, J.L. Serrano and M.A.Perez-Jubindo, *Liq. Cryst.*, 18, 751 (1995).
- 63 R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. de Phys. Lett.*, 36, 69 (1975); N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, 36, 899 (1980).
- 67 N. A. Clark, M. A. Handschy and S. T. Lagerwall, *Mol. Cryst. Liq. Cryst.*, 94, 213 (1983).
- 65 S. T. Lagerwall, B. Otterholm and K. Skarp, *Mol. Cryst. Liq. Cryst.*, 152, 503 (1987); L. S. Beresenev, L. M. Blinov, M. A. Osipov and S. A. Pikin, *Mol. Cryst. Liq. Cryst.*, **158A**, 1 (1986).
- 66 J. W. Goodby, E. Chin, T. M. Leslie, J. M. Geary and J. S. Patel, *J. Am. Chem. Soc.*, 108, 5210 (1986); D. M. Walba, S. C. Slater, W. M. Thurmes, N. A. Clark, M. A. Handschy and F. Supon, *J. Am. Chem. Soc.*, 108, 5210 (1986).
- 67 R. B. Meyer, *Mol. Cryst. Liq. Cryst.*, 146, 151 (1977); P. Keller, L. Liebert and L. Strzelecki, *J. de Phys. Lett.*, 37, 3 (1976).
- 68 M. Luzar, V. Rutar, J. Selinger and R. Blinc, *Ferroelectrics*, 58, 115 (1984).
- 69 J. S. Patel, J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 144, 117 (1987).
- 70 K. Yoshino, M. Ozaki, T Sakurai, K. Sakamoto and M. Honma, *Jap. J. Appl.*

- Phys., 23, L175 (1984).
- 71 B. Otterholm, C. Alstermark, K. Flatischler, A. Dahlgreen, S. T. Lagerwall and K. Skarp, *Mol. Cryst. Liq. Cryst.*, 146, 189 (1987).
 - 72 L. J. Yu, H. Lee, C. S. Bak and M. M. Labes, *Phy. Rev. Lett.*, 36,388 (1976); S. S. Bawa, A. M. Biradar, K. Saxena and Subhas Chandra, *Rev. Sci. Instrum.*, 59, 2023 (1988).
 - 73 P. Pieranski, E. Guyon and P. Keller, *J. de Phys.*, 36, 1005 (1975); K. Skarp, I. Dahl, S. T. Lagerwall and B. Stebler, *Mol. Cryst. Liq. Cryst.*, 114,283 (1984).
 - 74 K. Miyasato, S. Abe, H. Takezoe, A. Fukuda and E. Kuze, *Jap. J. App. Phy.*, L661 (1983), and references cited therein.
 - 75 A. J. Leadbetter, in *The Molecular Physics of Liquid Crystals*, ed. G. R. Luckhurst and G. W. Gray, Academic Press, New York, Chapter 13.
 - 76 G. R. Mitchell, F. J. Davis and A. Ashman, *Polymer*, 28,639 (1987); L. V. Azaroff, *Mol. Cryst. Liq. Cryst.*, 145, 2280 (1987).
 - 77 P. Martinot-Lagarde, R. Duke and G. Durand, *Mol. Cryst. Liq. Cryst.*, 75, 249 (1981).
 - 78 J. S. Patel and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 144, 117 (1987).