THE UNIVERSITY OF HULL

# SIDE CHAIN LIQUID CRYSTAL POLYSILOXANES

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by

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# ABSTRACT

Laterally attached side chain liquid crystal polymers (SCLCP), which involve the appendage of the calamitic mesogenic group to the backbone *via* a flexible spacer in such a way that the axis of the rod-like group lies in the direction of the backbone, were first synthesised only a few years ago. As the characteristics of this new class of SCLCP are still not well defined, the preparation of laterally attached SCLCP was first examined, so that a reliable and reproducible method could be developed to synthesise side chain homopolymers and copolymers, derived from commercially available, preformed polysiloxane backbone homopolymers and copolymers. The factors which affect the synthesis of these materials were systematically investigated, and the polymers have been fully characterised both by analytical techniques and by physical study.
The important effects of molecular weight and polydispersity of the SCLCP on phase transition temperatures are fully discussed.

Using novel mesogenic groups with an unusually asymmetric point of linkage along the molecular long axis to bond the side chain to the polymer main chain *via* the flexible spacer, a range of laterally attached SCLCP has been synthesised to allow the establishment of structure-property relationships. The research was geared towards the production of SCLCP that exhibit room temperature nematic phases with positive dielectric anisotropies, by the use of terminally cyano-substituted mesogenic groups, since such materials are of potential interest for speciality applications. Much effort was therefore spent on maximising the dielectric properties of the resultant polymer.

In addition, a study of side chain copolymers with terminally and laterally attached side chains has been conducted, and these mixed copolymer systems were found to offer greater control and flexibility over the fine tuning of liquid crystalline properties.

## LECTURE PRESENTATIONS

1. Novel laterally attached side chain liquid crystal polysiloxanes with room temperature nematic phases.
   M.S.K. Lee, G.W. Gray, D. Lacey and K.J. Toyne, 4th British Liquid Crystal Society Annual Conference, Sheffield, 1989.

2. Molecular weight effects on side chain polysiloxanes and the properties of polysiloxanes with mixed lateral and terminal side chains.
   M.S.K. Lee, G.W. Gray, D. Lacey and K.J. Toyne, 5th British Liquid Crystal Society Annual Conference, Bristol, 1990.

## POSTER PRESENTATIONS

1. The effect of changing backbone flexibility for laterally attached side chain liquid crystal polysiloxanes.
   M.S.K. Lee, G.W. Gray, D. Lacey and K.J. Toyne, 5th British Liquid Crystal Society Annual Conference, Bristol, 1990.

2. New co-polysiloxanes incorporating laterally and terminally attached mesogenic side groups.
   G.W. Gray, J.S. Hill, D. Lacey and M.S.K. Lee, 13th International Liquid Crystal Conference, Vancouver, 1990.

3. X-ray diffraction from laterally attached side chain liquid crystalline polymers.
   A.S. Cherodian, R.M. Richardson, M.S.K. Lee and G.W. Gray, 6th British Liquid Crystal Society Annual Conference, Reading, 1991.

# PUBLICATIONS

1. Aspects of side chain liquid crystal polymers, especially polysiloxanes, in relation to their potential for speciality applications.
   G.W. Gray, W.D. Hawthorne, J.S. Hill, D. Lacey, M.S.K. Lee, G. Nestor and M.S. White, *Polymer*, **30**, 964 (1989).

2. Polysiloxanes with laterally attached side chains bearing terminal cyano groups.
   M.S.K. Lee, G.W. Gray, D. Lacey and K.J. Toyne, *Makromol. Chem., Rapid Commun.*, **10**, 325 (1989).

3. The effect of diluting polar terminal groups with non-polar terminal groups in laterally attached side chain copolymers.
   M.S.K. Lee, G.W. Gray, D. Lacey and K.J. Toyne, *Makromol. Chem., Rapid Commun.*, **11**, 109 (1990).

4. The effect of changing backbone flexibility for laterally attached side chain liquid crystal polysiloxanes.
   M.S.K. Lee and G.W. Gray, in preparation.

5. R.D.C. Richards, J. Hollingshurst, M.S.K. Lee, J.A. Semlyen and G.W. Gray, in preparation.

6. A.S. Cherodian, R.M. Richardson, M.S.K. Lee and G.W. Gray, in preparation.

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## 1.1 GENESIS

Combining the virtues of low molecular mass liquid crystals with the properties of polymers is an extremely exciting concept, and this is realised in the production of liquid crystal polymers. The ability to exploit the characteristics of both systems -- the thermal mesomorphic behaviour of liquid crystals and the mechanical attributes of polymers -- has meant that research into liquid crystal polymers has been very actively pursued both from an academic and a commercial viewpoint.

Long before the discovery of liquid crystal polymers, much was known about the phenomenon of liquid crystallinity, which dates back to the observations of Reinitzer [1] who, in 1888, noticed that cholesteryl benzoate melted at 145 °C to give a mobile but turbid fluid. This became a clear, isotropic liquid, but only when heated to 179 °C. Lehmann [2], working quite independently, was able to corroborate these results a few years after, but it was only through Friedel [3] in 1922, as a result of his extensive work in optical microscopy, that these observations on this intermediate state or mesophase were accepted as relating to the properties of a quite new and different state of matter. This led to the coining of the term liquid crystal, which is in itself quite self-explanatory and accurate. It appropriately brings to mind the properties of a liquid -- the ability to flow, and the properties of a crystal -- the existence of order. Matter is normally classified under three distinct states, namely the solid state, the liquid state and the gaseous state. The fact that liquid crystals do not fall conveniently into any of these three categories, since they are neither truly crystalline nor truly liquid, but have properties intermediate between these two states, is regarded by some as justification for liquid crystals being recognised and acknowledged as the fourth state of matter [4].

In comparison, the history of liquid crystal polymers (LCP) is still in its infancy. Studies were first centred on liquid crystalline main chain polymers, which date back to the early work of Onsager [5] in 1949 and of Ishihara [6] in 1950 concerning theoretical interpretations of the packing of rigid rod-like molecules. This theory was extended by

Flory [7] in 1956, who proposed that macromolecules should be able to form a lyotropic liquid crystalline phase above a critical concentration in a solvent. As a result of these conclusions, interest was generated in the incorporation of liquid crystalline moieties, i.e., molecular units structurally similar to the molecules of low molecular mass (LMM) materials known to form liquid crystal phases, into a macromolecular system. Eventually this led to a strong upsurge in LCP work, especially over the last twenty years. This is evidenced by the increased numbers of publications on both pure research as well as on technological applications, the latter a result of the realisation of the commercial potential of LCP. However there is still much more to be learned about the subject, and the sustained financial investment in LCP research both at academic and industrial establishments is witness to this fact.

## 1.2 LIQUID CRYSTAL POLYMERS

The work for this thesis has centred upon the preparation and study of a range of novel liquid crystal polymers. To keep this Introduction within reasonable bounds of length, the background information provided has been kept very specific to liquid crystal polymers, and only those aspects of low molecular mass liquid crystals and of polymer science in general that are relevant to the main subject matter of this research, i.e., liquid crystal polymers, have been incorporated.

### 1.2.1 Definitions

The terminology commonly used in the area of liquid crystal polymers is first defined [8]. A *polymer* is effectively a large (often long) molecule or macromolecule, which is produced as the result of various types of polymerisation reaction. These are the processes whereby individual monomer units react chemically together to form either extended chains or a 3-dimensional network of interlinked polymer chains. If only one type of monomer is employed in the polymerisation reaction, the resulting polymer is known as a *homopolymer*. A *copolymer* is obtained if more than one monomer species is used in the formation. In addition, both *statistical* and *block* copolymer systems may be envisaged, and these terms refer respectively to the different types of copolymer in which the monomer species occur randomly and in segments or blocks (sometimes regular) consisting of only one of the monomer species involved.

Each polymer consists of many covalently bonded monomeric units. There is a need to quantify the size of the macromolecule, and this is normally done by quoting the molar mass (M) of the polymer. An associated parameter which is often used is the *degree of polymerisation* (DP), and this is simply the number of monomeric repeat units in the polymer molecule. This is defined as:

$$DP = M/M_0$$

where $M_0$ is the molar mass of the monomer.

It is difficult, of course, to quote the true molar mass of a real polymer sample since it normally contains molecules with a variety of chain lengths. When a spread of molar mass occurs, the polymer sample is said to be polydisperse. Unless a monodisperse situation can be achieved, i.e., where the polymeric material is confined to having chains that are identical in molar mass or which lie within a narrow range of molar masses, an average value of the molar mass must be quoted. This value can either be a *number average molar mass*, $\overline{\mathrm{Mn}}$, or a *weight average molar mass*, $\overline{\mathrm{Mw}}$. Using these values, the extent of the molar mass distribution or the *polydispersity* ($\gamma$) is defined by the heterogeneity index, $\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$. A monodisperse system has a polydispersity close to unity ($\overline{\mathrm{Mw}} = \overline{\mathrm{Mn}}$), but more typically, $\gamma$ values may range between 2 and 20. The degree of polymerisation too is normally expressed as an average value ($\overline{\mathrm{DP}}$).

In the context of LCP, the temperature at which a non-crystallising polymer changes from isotropic liquid to isotropic glass on cooling is known as the Tg or glass transition temperature. The reverse process occurs on heating. Below this temperature, the polymer backbones no longer have sufficient energy to slide over one another, but, although the glass is rigid, it is not a true ordered solid. If however the polymer exhibits an enantiotropic mesophase above Tg, then the glass obtained on cooling is an anisotropic glass. This is because the anisotropic orientations of the mesogenic units are not affected on cooling through Tg, and so the structure and texture of the mesophase are maintained in the glassy state.

### 1.2.2 Mesophases

When a normal organic crystalline solid melts, it does so in a single process, with the breakdown of the 3-dimensional, long range positional and orientational order of its constituent units. The abrupt collapse of this lattice array to form the isotropic liquid gives way to free rotation and translation of the molecules, i.e., to a zero order state. The temperature at which this transformation takes place is known as the melting point.

However, in systems where the molecules are lath-like or rod-like, the change to a zero order state need not be complete in one step. Instead, such compounds may melt to give rise to intermediate states which exist on a temperature scale intermediate between the ordered crystal and the disordered isotropic liquid; these states are known as liquid crystal phases or mesophases (Figure 1.1). This happens as a result of the anisometric nature of fairly rigid, elongated molecules, which allows retention in some degree of the long range orientational order of the molecular long axes. The molecules will then have lost their long range positional order and have retained only long range orientational order.

Liquid crystalline materials which exhibit mesophases on heating or cooling are known as thermotropic liquid crystal materials or mesogens. In addition, there are other types of phase which are intermediate in their degree of order between that of the crystalline solid and the disorder of the isotropic liquid. These are called lyotropic liquid crystal phases [9], and develop from amphiphilic compounds which form mesophases in the presence of an appropriate concentration of a specific solvent, often water. Amphiphilic moieties may be incorporated into LCP and give rise to very interesting polymeric systems, but their study was not part of this work. No further mention of lyotropic systems will therefore be made in this thesis.

Plastic crystals too are of interest in the present context concerning the way in which order is lost on heating a 3-D ordered crystal lattice [10]. In these cases, the crystal lattice is composed of roughly spherical molecules, and at some particular temperature, the molecules become able to rotate freely, but retain position on their lattice sites. Local positional order is therefore lost, but the long range ordering of the molecular centres of gravity is retained until a higher temperature transition to the isotropic liquid. Plastic crystals are again not a feature of this research, and no further mention of them is made in this thesis.

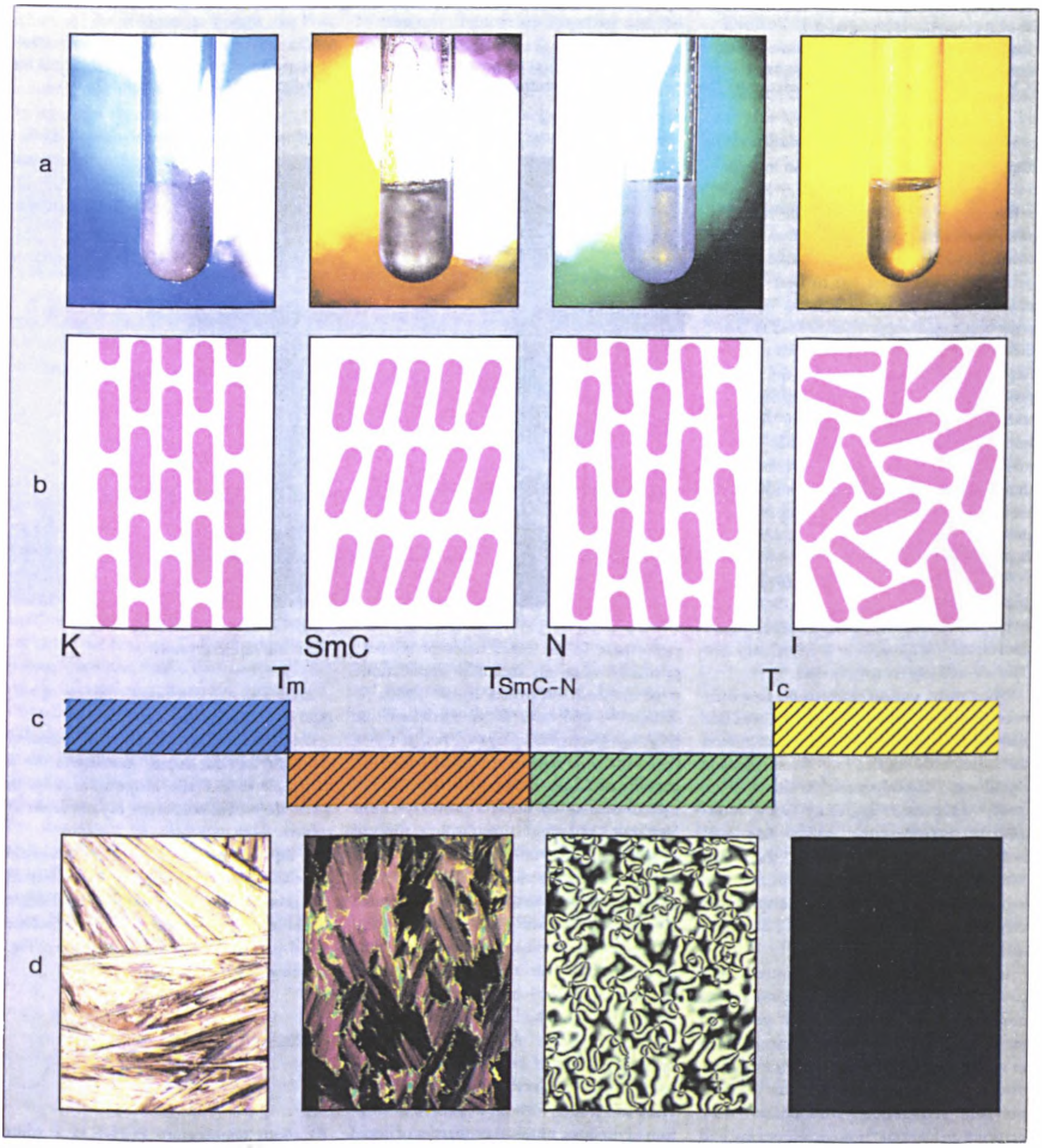


*Figure 1.1*
***Illustration of different states of aggregation.***

*1.1a shows, from left to right, the macroscopic appearance of a liquid crystal material, below the melting point Tm, in its crystalline state, a smectic C liquid crystalline phase above the melting point, a nematic liquid crystalline phase at increased temperature, and the isotropic phase above the clearing point Tc.*
*The diagrams in 1.1b schematically represent the respective microscopic ordering in these various states.*
*1.1c represents the corresponding thermotropic phase diagram, using the usual convention.*
*1.1d gives the textural appearances of the different states as seen through a polarising microscope; from these it is possible to assign the phases to specific liquid crystalline classes for given materials. The isotropic state appears black between crossed polarisers.*

[Reproduced from *Kontakte*, 2, 8 (1988)]

In comparison to LMM systems, LCP are rather more highly ordered, since the mesogenic groups are appended to or incorporated in the polymer backbone. It is envisaged however that with sufficient decoupling of the mesogenic moieties, through the use of flexible spacers, the behaviour of mesogenic groups in the mesophase ordering of polymers is similar to that in low molecular weight analogues. An equivalent phase classification is therefore used to define mesophase types, and to date, many known LMM phases have also been observed for LCP.

Mesophases are most conveniently identified by polarising optical microscopy, as phase assignment is possible through the correct recognition of the textures that are formed. These textures are characteristic for the birefringent patterns of the phase types, which are viewed microscopically as thin films between glass surfaces, using a polarising microscope and crossed polarisers.

As a result of his optical microscopic studies on LMM liquid crystal materials [3], Friedel discovered that the textures of <u>each</u> type of phase depend intrinsically on:

(i) the nature of the compound that gives rise to the mesophase;

(ii) whether the mesophase is formed on heating the solid or another mesophase, or as a result of cooling from the isotropic liquid;

(iii) the nature of the supporting surfaces.

Furthermore, changes between different textures can be induced by external forces, and this allows the optical properties to be easily changed. A brief explanation of the possible microscopic textures that are commonly obtained for each phase type follows the appropriate section in this chapter.

### 1.2.2a Identification

A major problem in the study of LCP is phase identification. The most common method used with LMM materials for this determination is polarised light microscopy. Due to the high viscosity of polymeric materials, the broad spread of molecular weights, the biphasic nature of the liquid crystal melt near phase transitions, and possible interferences in mesophase ordering by the polymer backbone, the assignment of mesophase type by optical microscopy is however more difficult than for LMM materials. The textures of polymeric liquid crystals are, for example, normally not well defined without prior annealing, the process by which a thin layer of the mesophase is held for periods of several hours or even days at a constant temperature just below its upper transition temperature, e.g., the clearing point. At times, prolonged annealing may still not give recognisable textures, and in these situations, other techniques have to be sought to determine the phase type.

Miscibility studies are used extensively in LMM work to identify phase types [11]. These are based on the concept of continuous miscibility between identical phases over an entire binary composition range. The miscibility concept has also been demonstrated both for main chain [12] and side chain [13] LCP in some binary mixtures with LMM materials, but only for the nematic phase, with which total miscibility has been observed. However, miscibility cannot be used for the classification of the smectic phases of polymers, due to immiscibility in most cases between high and both high and low molar mass materials. This problem of immiscibility exists even between materials of the same phase type and of similar chemical structure [13]. As a consequence, miscibility methods for phase classification are rather limited in their applicability in the field of LCP.

Thermal analysis (Differential Scanning Calorimetry [DSC] and Thermal Optical Analysis [TOA]), the most common techniques used in the characterisation of LCP, supply information regarding the temperatures at which phase transitions occur. From DSC, the magnitude of the enthalpy change accompanying each phase transition is obtained and this can be useful to differentiate between a nematic-isotropic and a smectic-isotropic phase transition, due to the different degrees of order for the two phases. $\Delta H$ for $T_{S-I}$ is much greater than $\Delta H$ for $T_{N-I}$. However, it is not possible to tell from these results the nature of the smectic phase involved.

X-ray diffraction is often the only definitive tool for proving mesophase type in a LCP. The results from such a study can allow the detection of any layered arrangement and also give information about the molecular arrangement within the layers [14]. The diffraction patterns, when interpreted, can thus be used to confirm the phase type suspected *via* a combination of the other techniques listed above, or in difficult cases, provide evidence for a particular type of phase. However problems are inherent with this method as well, most significantly those of obtaining well aligned sample preparations for x-ray analysis.

There are two major classes of liquid crystal phase, smectic phases and the nematic phase, and this classification reflects the different degrees of order for the two systems. Smectic mesophases are viscous, turbid phases which consist of layers of molecules. Due to the structural analogy between a smectic layered system and that of a soap film consisting of orientated amphiphilic molecules, the phase was designated smectic, the term being derived from the Greek for soap-like -- *smectos*. On the other hand, the nematic phase is very much more mobile. In the bulk, it is turbid, but when viewed under the microscope, it has a shimmering appearance due to Brownian motion. When observed microscopically between crossed polarisers, thick samples of the phase often adopt a 'threaded' texture; mobile, black threads (optical discontinuities) pervade the film. It was because of this property that the phase was named nematic -- the Greek for thread-like is *nematos*. In addition, there is another phase, the cholesteric phase, which is also referred to as the chiral nematic or spontaneously twisted nematic phase, and this is best thought of as a sub-class of the nematic state. This phase is formed only by compounds that are optically active. The cholesteric phase, like the nematic phase, is quite mobile and turbid in nature, although the optical activity of the mesogen imparts unique optical properties to the system that are absent in nematics, e.g., in appropriate cases, the ability to give selective reflection of coloured light in a narrow wavelength band which is dependent upon temperature. The term cholesteric was originally used to describe this phase, since, at that time, the majority of compounds exhibiting this phase were derivatives of cholesterol.

### 1.2.2b The Smectic Phase

The smectic phase is characterised by the parallel arrangement of molecules in layers. In fact, the system can be thought of as 2-dimensional layers stacked over each other with well-defined spacings, the layers having different degrees of freedom of movement with respect to each other in true smectics. This is possible, because heating has only dispensed with the terminal intermolecular forces, the lateral forces still being very evident and holding the molecules in a layered structure. Furthermore, the molecular long axes in each layer may be positioned orthogonal to the layer plane or tilted at an angle.

There are presently twelve different smectic types, assigned as $S_A$ through to $S_K$ (there are two forms of B phase, the hexatic smectic B and the crystal B phases). This rich polymorphism arises from the different orientations of the molecules within the layers and the different types of ordering of the molecules within layers and from one layer to the next, i.e., there may be some long range inter-layer ordering or a random inter-layer arrangement of the molecules (Figure 1.2). When positional order is retained through stacks of layers, in addition to the long range order within the layer planes, the phases are very ordered and have recently been termed crystal smectic phases. These in fact have 3-dimensional order, but are soft crystals with low shear stress between the layers -- the crystal smectic phases are B, E, G, H, J and K. The true smectic phases lack positional correlations between layer planes; these are the true smectics -- A, C, F, I and hexatic B. There is an additional phase contained within the smectic classification, the D phase, but this is really an anachronism. It is now known that the D phase does not have a layered structure. Instead, it has a cubic structure and is optically isotropic, and so strictly it should be in a class of its own.

With so many different smectic phases, it is not surprising to find that a particular microscopic texture can exist for two or more smectic forms. Furthermore, each smectic

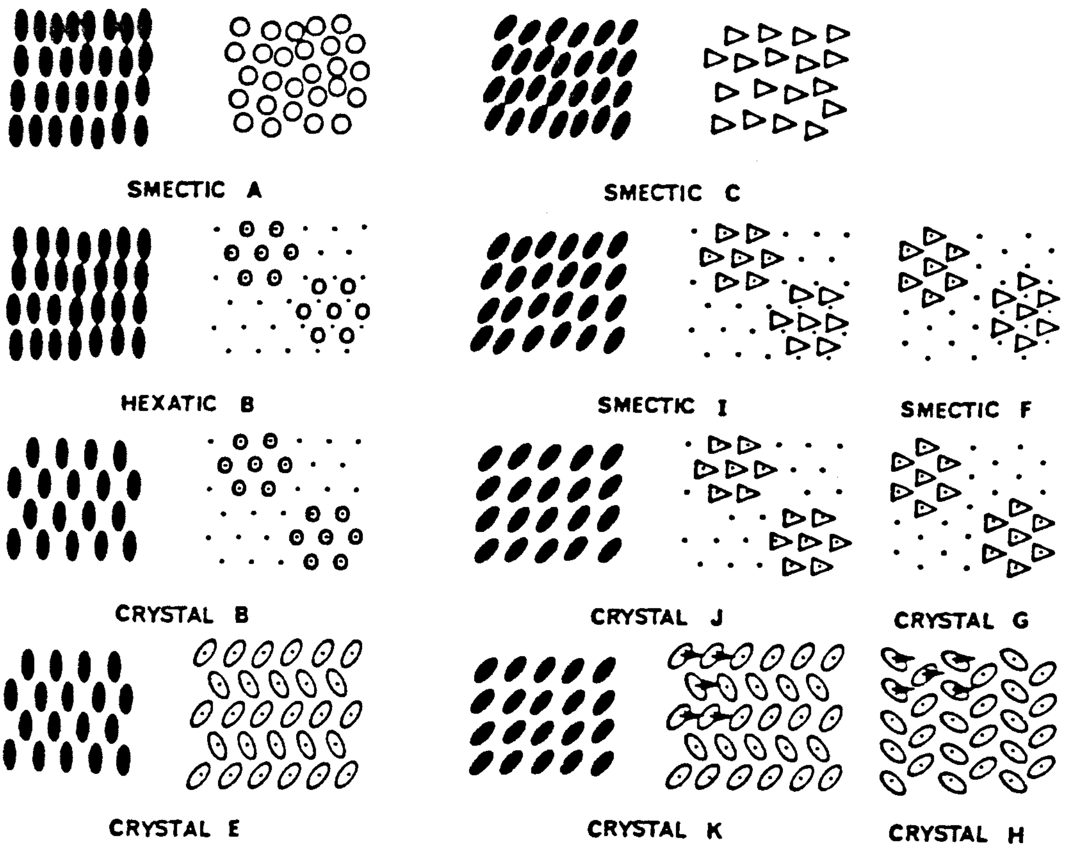


***Figure 1.2***
***Diagramatic representation of the structures of the different polymorphic smectic modifications.***

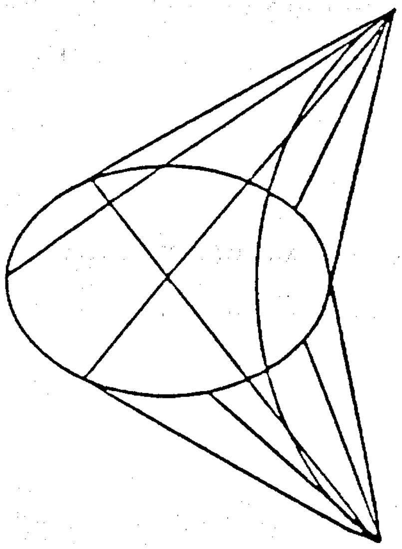
*For each modification, the smectic structure is depicted in elevation (left) and in plan (right).*
*In the plan representations, the molecules are shown either as*
*(i) circles (rotational freedom);*
*(ii) triangles (rotational freedom but tilted with respect to apex or side of the hexagonal net);*
*(iii) ellipses (restricted rotation) -- if tilted, the tilt direction is shown by arrows.*
*Points represent lattice points for the perfect geometrical net.*

[Reproduced from *"Smectic Liquid Crystals: Textures and Structures"*, by G.W. Gray and J.W. Goodby, Leonard Hill, Glasgow (1984)] phase type can exhibit a number of different textures. The subtle differences which occur at some phase transitions make recognition difficult to the inexperienced eye. To try and describe every possible texture for each smectic phase type is beyond the scope of this thesis, and the information is best obtained by referring to a specialised text [15]. Instead, the main microscopic textures encountered in the study of smectic polymorphism are summarised, these being the homeotropic texture (molecules are aligned perpendicular to the glass surfaces, giving a phase which is optically extinct), the focal-conic or fan texture (obtained on cooling from the isotropic liquid and initially observed as elongated particles termed bâtonnets, which then coalesce to form this texture -- Plate 1), the homogeneous texture, the mosaic texture, and the schlieren texture (Plate 2) -- these last few textural forms are very similar to those exhibited by the nematic phase and are discussed in Section 1.2.2c.

The focal-conic or fan texture must however be mentioned (Plate 1). This arises when the smectic layers are no longer flat, but curved. It was first realised by Friedel [3] that a volume of space can effectively be filled by focal-conic domains defined by an ellipse and a hyperbola related as a focal-conic pair, i.e., the hyperbola passes through one focus of the ellipse and lies in a plane at right angles to the plane of the ellipse (Figure 1.3). The volume of a focal-conic domain -- a pair of cones, when the ellipse becomes a circle and the hyperbola is then a line through the centre of the circle, at right angles to the plane of the circle -- can be filled by equidistant, curved, parallel strata, and the bulk phase is derived from a packing of these domains with a continuum of the parallel strata running through it. Discontinuities in the system are then the ellipses and the hyperbolae, and these can be seen as black lines (optical discontinuities) in a texture which consists of fan-like regions formed when the growing focal-conic regions encounter the glass supporting surface. The texture is very typical for the $S_A$ phase and is formed on cooling from the isotropic liquid. The focal-conic texture also occurs on cooling with other smectics, often paramorphotically, because the texture develops from a focal-conic $S_A$ phase already existing at a higher temperature.

*Figure 1.3*

*The focal-conic domain of a smectic phase*



As highlighted earlier, there is a problem in obtaining clear, distinguishable microscopic textures for LCP that are truly characteristic of the phase type, and this has meant that identification by optical microscopy is extremely subjective and at times even misleading.

### 1.2.2c The Nematic Phase

On heating a smectic phase to a sufficiently high temperature, the strong lateral forces can weaken, leading to the formation of either the isotropic liquid or the nematic phase. Unlike the smectic phase, there is only one nematic phase. As only weak lateral forces remain, there is no layered structure associated with the nematic phase. Instead, the molecules are aligned roughly parallel to a preferred direction defined by a parameter called the director (**n**). This long range, parallel, orientational order of the molecular long axes occurs throughout the bulk of the phase; although the director may change dramatically in orientation from one position to another in the bulk phase, it always does so continuously except at defects which are identifiable microscopically in thin films. Due to the absence of a layered structure, the nematic phase is more mobile than the smectic phase, and is thus more akin to the isotropic liquid.

The high degree of fluidity of the nematic phase can be seen microscopically; a thin film of the nematic preparation viewed between crossed polarisers appears to shimmer. This effect is caused by the Brownian motion of the molecules. The characteristic feature of the phase is the manner in which a wavefront of spherical birefringent droplets of the nematic phase sweeps across the field of vision when the phase forms by cooling from the isotropic liquid. This then gives what is often a colourful texture from what was initially the black, optically extinct isotropic liquid. This coalescence of the droplets within a short temperature range may in fact form one of several possible characteristic textures, the nature of which depends on the structure of the mesogen, the condition/nature of the supporting surface and the thickness of the preparation being viewed.

Depending on attractions between the molecules and the glass surfaces and/or by the application of certain alignment techniques, it may be possible to produce textures of either homeotropic or homogeneous alignment. A homeotropic texture is obtained when the interactions between the molecules and the glass are weak. The molecules and hence the director are oriented perpendicular to the glass support, and the plane polarised light passes along the long axis of the molecule without being refracted. This gives a phase that is optically extinct when viewed between crossed polarisers. The preparation can be made to flash and show birefringence briefly when the cover slip is touched. This causes the film to scatter momentarily and exhibit a birefringent texture, which then rapidly re-orientates to its orthogonal arrangement. On the other hand when the attractions between the molecules and the glass are strong, the molecules are able to lie horizontally on the glass. With the molecules now normal to the incident light, an even birefringence is produced. These two uniformly aligned states may be rapidly interchanged, when the dielectric anisotropy is appropriate, on application of an external electric field. This ability to switch from one stable, uniformly aligned state to another forms the basis of electro-optic display devices, in which nematic liquid crystals have been extensively utilised.

Another commonly occurring texture is the schlieren texture, of which there are a number of varieties, and these have been categorised accordingly [16]. This texture is usually formed on heating the nematic phase to just below its transition to the isotropic liquid. The texture is extremely birefringent, but also exhibits optically extinct 'string-like strands' (Plate 3). These are in fact distorted crosses of extinction, which centre around points or lines of optical discontinuity (disclinations). The black bands, which emerge from the centres of these crosses, are referred to as 'brushes'. A nematic phase may contain centres with either two or four 'brushes' -- see Figure 1.4. The schlieren texture can also occur with certain smectics, e.g., smectic C (Plate 2). However in these cases, the centres always exhibit four 'brushes', and this allows for a distinction of the smectic schlieren texture from that displayed by the nematic phase.

In addition, there are a further two nematic textures which are not as frequently observed. The threaded texture, from which the phase obtained its name, is a birefringent texture that contains many thin, sharply defined lines or threads which have no particular geometric shape. The threads represent optical discontinuities associated with rotation of the director. The marbled texture, on the other hand, appears as a background with large weakly birefringent areas. This is due to imperfectly homeotropically aligned molecules generating areas exhibiting different shades of grey arising from slightly different orientations of the optical axis.

In liquid crystal polymers, the nematic texture most frequently encountered is the homogeneous texture. As a result of the polydispersity and viscosity of the preparation, the nematic-isotropic transition of a LCP is often not as precisely reversible on heating and cooling as that of a low molar mass nematic. Moreover, instead of the shimmering nematic droplets which are observed when a low molar mass nematic is obtained on cooling from the isotropic liquid, the LCP nematic phase may develop as a uniform birefringence of gradually increasing brightness and contrast over quite a broad temperature range. Furthermore, there is often a certain amount of supercooling at the transition. A similar problem is obtained on heating the phase to the isotropic melt.

The gradual fading of the texture often makes it difficult to assign a precise value to the isotropisation temperature by optical microscopic techniques. As such, differential scanning calorimetry (DSC) is often used to obtain the clearing point, and this is taken as the maximum of the endothermal peak of the thermal analysis trace, although this peak is usually much broader than that for low molar mass nematics, again as a consequence of the polydispersity.

### 1.2.2d The Cholesteric Phase

Molecules that form the cholesteric phase (now frequently referred to as the chiral nematic phase) are structurally very similar to those that give a nematic phase. The only difference is that in the former case, the molecules are chiral, i.e., they are optically active.

However the structure of the cholesteric phase itself is very different to that of the nematic phase (Figure 1.5). When appropriate thin slices taken through the bulk of this phase are considered, it can be seen that the molecules in each slice are orientated in a very similar fashion to that found in the nematic phase. However, the director is rotated slightly between neighbouring slices, and the cumulative effect up through a stack of slices gives a turning of the director through 360°, i.e., a helical structure exists that has a pitch which can be measured. This property exists due to the molecular asymmetry, and the helix may exhibit a left- or right- handed form according to which optical enantiomer of a given material is under consideration. A nematic mesophase can be 'made' cholesteric by doping with only small amounts of an optically active compound, which may not even necessarily be mesogenic. The structure of the nematic phase may indeed be thought of as being a helix of infinite pitch length, to which the addition of trace amounts of a chiral dopant effectively imparts a helical structure with a long pitch length. This explains why optical isomers of a given cholestrogen exhibit identical cholesteric properties, but with opposite helical twists, yet show only nematic properties in the racemic system. With the helices being of opposite handedness in the pure optical enantiomers, the nett effect in such systems is one of cancellation and this produces an infinite pitch length helix. Perhaps it is then not surprising to note that the cholesteric to isotropic transitions for optical isomers occur at the same temperature as the nematic clearing temperature for the racemic system [17].

As a result of the helical nature of the phase, light incident upon a thin film of a cholesteric phase with the helical axes orthogonal to the supporting surfaces sees a set of equally spaced layers. The result is a selective Bragg type reflection of light in a narrow wave band. For viewing down the helical axes, $\lambda = np$ ($\lambda$ = wavelength of light reflected, $n$ = average refractive index of the cholesteric and $p$ = the pitch length) and therefore cholesteric liquid crystals can selectively reflect light of different wavelengths and display different reflectance colours if the helix pitch is in the wavelength range of visible light (n being considered as approximately 1). The colour of the light reflected may be influenced thermally, since the pitch length is, in most cases, sensitive to temperature change. A decrease in temperature normally causes the wavelength of reflected light to change from the ultra-violet, through the visible spectrum, and into the infra-red region. It is this property which makes cholesteric liquid crystals useful as sensitive thermochromic materials, particularly as, for suitable materials, the entire colour play occurs over less than a degree centigrade.

Like the nematic phase, there is only one cholesteric phase type, and this can exhibit two distinct microscopic textures. The cholesteric phase can either adopt a focal-conic texture (Plate 4), or, when aligned, with the helices orthogonal to the surfaces, it may also give the colour reflecting planar or Grandjean texture [18]. When the cover slip is touched, the focal-conic texture changes to the planar texture.

*Figure 1.4*

*Nematic schlieren 'brushes' which may emanate from centres characterised by either*
*(a) two 'brushes' or*
*(b) four 'brushes'*

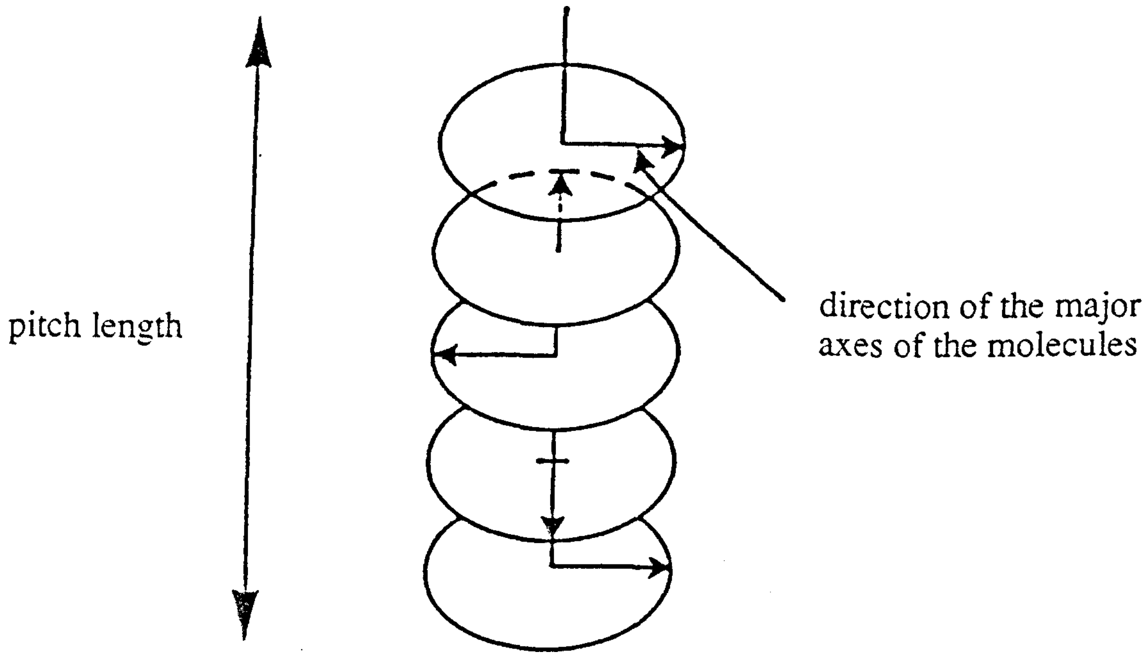


*Figure 1.5*

*The cholesteric helix*

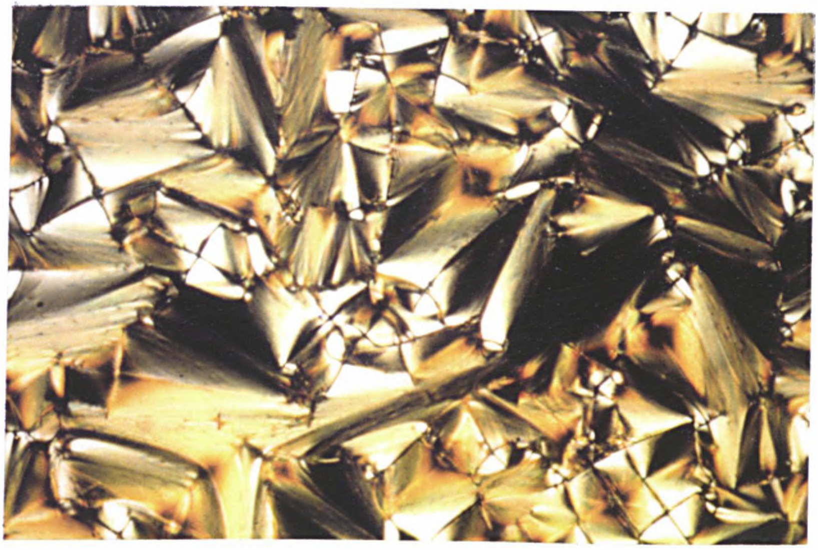


***Plate 1***

*The focal-conic fan texture of the smectic A phase*

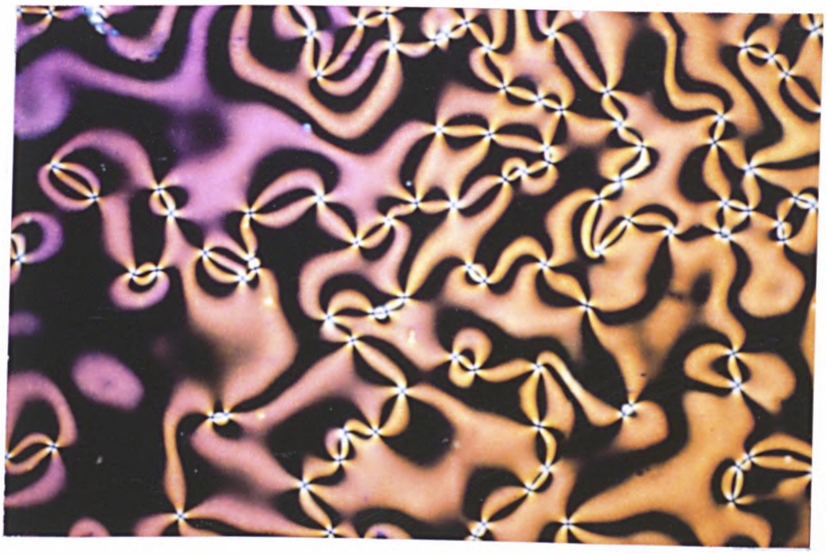


***Plate 2***

*The schlieren texture of the smectic C phase*

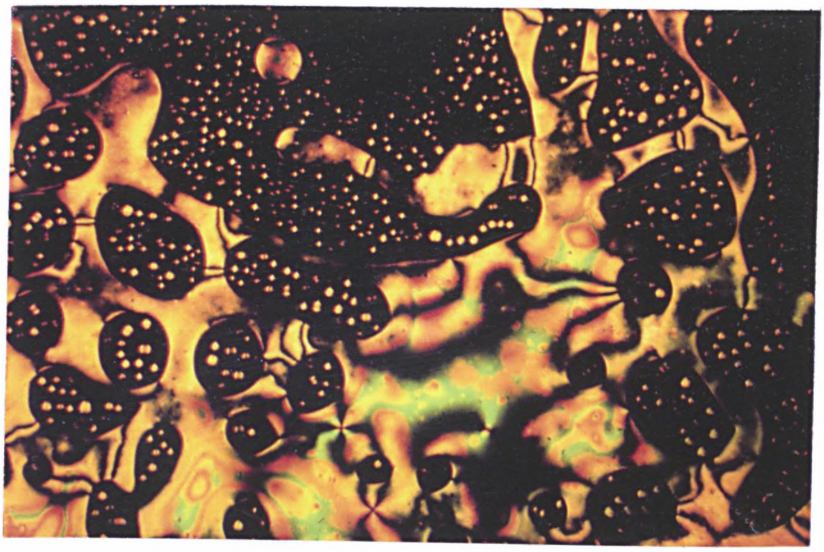


**Plate 3**

*Nematic droplets and schlieren texture of the nematic mesophase*

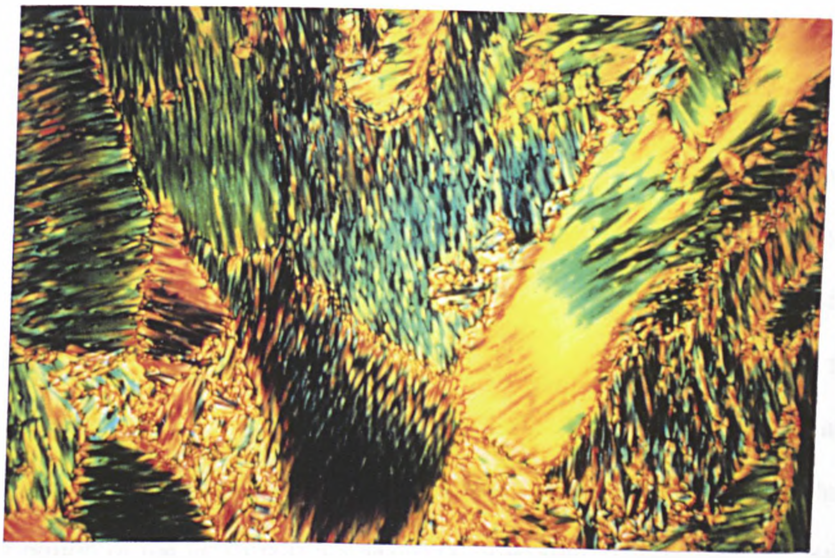


**Plate 4**

*The focal-conic texture of the cholesteric mesophase*

In addition, cholestrogens of suitable pitch length are able to exhibit other phases known as 'blue phases'. These exist over a narrow temperature interval and may be observed optically on cooling from the isotropic liquid, but before the focal-conic texture of the cholesteric phase develops. There are currently three identified types of 'blue phase', appropriately termed 'blue phase I', 'blue phase II' and 'blue phase III' [19], and these differ only slightly in their textural appearance.

### 1.2.2e Ferroelectric Mesophases

Some materials possess two or more spontaneously polarised orientational states in the absence of an applied field, and can be transformed from one orientational state to the other by the application of an electric field. These materials are said to be ferroelectric, and of the twelve basic smectic phases identified, only the seven tilted phases are in theory of sufficiently low symmetry to exhibit ferroelectric properties, and only then if their constituent molecules are optically active or the phases have been doped with a chiral dopant [20].

In the uncorrelated tilted smectic phases, i.e., $S_C$*, $S_F$* and $S_I$*, the chirality of the molecules causes the tilt direction to rotate continuously on passing through a succession of layers in the bulk of the phase, developing another type of helical structure, analogous in some ways to the helical property of the cholesteric phase. In each layer of the $S_C$* phase there is a macroscopic dipole, i.e., a spontaneous polarisation running through the layer plane at right angles to the tilt plane. Obviously, because of the helical arrangement, the nett polarisation of each individual layer is reduced to zero for the bulk phase, and the helical distribution of the tilt directions has to be unwound in order that the bulk phase consists of many layers with macroscopically useful ferroelectric properties which can be exploited. These arguments also apply to $S_F$* and $S_I$*. With the more crystalline smectic phases, i.e., $S_J$*, $S_G$*, $S_K$*, and $S_H$*, the long range inter-layer positional ordering of the molecules resist formation of the helical structure [21], and so the system should be truly ferroelectric. However for this behaviour to be observed, the tilt direction would have to be uniformly aligned throughout these crystal smectic phases, and this is never achieved practically, because the bulk phase or film forms different domains. Although each domain is ferroelectric, the bulk phase exhibits no nett ferroelectric properties.

Ferroelectric liquid crystalline polymers have only recently been synthesised, and these are claimed to exhibit the characteristics of spontaneous polarisation and surprisingly, very fast switching times; these switching times were several magnitudes smaller than conventional switching times for high viscosity nematic LCP [22, 23]. These results, which await confirmation, were for a chiral $S_C$ phase, the only ferroelectric mesophase that has been positively identified to date for LCP.

### 1.2.2f Phase Sequences

A crystalline solid which consists of fairly rigid elongated molecules may on heating form a nematic phase. Further heating would eventually give an isotropic liquid. If the molecules are optically active, the phase observed is the chiral nematic (cholesteric) phase. It is also possible that a smectic phase is first obtained on heating the crystal, especially if this possesses a layered structure, and the smectic phase may then be transformed into a nematic phase on further heating, before giving the isotropic liquid. Alternatively, the smectic phase may pass directly to the isotropic phase, without giving a nematic phase. Many materials of course exhibit more than one type of smectic phase and studies using a combination of techniques such as thermal analysis, optical microscopy, x-ray diffraction and miscibility studies have revealed that the most probable order of thermal stability for the twelve types of smectic phase is [24]:

$H < K < E < G < J < S_F <$ crystal $B < S_I <$ hexatic $B < S_C < D < S_A$

Only five or six of these smectic phases have been observed in a pure, single component system.

To summarise, the possible phase sequences are:

K --> N --> I

K --> S --> N --> I

K --> S --> I

where K = crystalline solid;

N = nematic phase, which is replaced by the cholesteric phase when the mesogen is chiral;

S = smectic phase or a sequence of smectic polymorphic modifications, the phase type being depicted by a subscript letter;

I = isotropic liquid.

The transformations mesophase-mesophase and mesophase-isotropic liquid are all precisely reversible. This means that the transition temperatures obtained from cooling and heating cycles are identical, with discrepancies between the two results normally being no more than 0.5 °C. Greater discrepancies indicate that the material is not pure. Temperature reversibility is an important characteristic of liquid crystals and is proof of the existence of a liquid crystal phase transformation. The situation is different for solid-solid, solid-liquid or solid-mesophase transitions, since supercooling normally occurs when the heating cycle is reversed.

For many liquid crystalline materials, the mesophase(s) may be observed both on heating and cooling cycles. These mesophases occur above the melting point of the crystalline solid and are said to be enantiotropic. However, if only observed on cooling the isotropic melt, the mesophases are said to be monotropic. This is possible because of the supercooling which can occur for the transformation to a solid. As such, monotropic phases always occur below the melting point of the solid. A given material may of course exhibit both enantiotropic and monotropic mesophases. For example, an enantiotropic nematic phase may form on heating the crystal, and on cooling, the nematic phase may form a monotropic smectic phase before crystallisation occurs.

### 1.2.3 Classification Of Liquid Crystal Polymers

A LC polymer may be considered as belonging to one of six different categories, based upon the type of mesogenic unit and the relationship of the mesogen to the polymer backbone. The mesogenic moiety can either be amphiphilic in nature, or non-amphiphilic, and in the latter case, there is a further subdivision. This depends upon whether the mesogenic moiety is rod-like (calamitic) or disc-like (discotic) -- liquid crystal phases may also be formed by disc-like shaped molecules. As the work for this thesis has involved only non-amphiphilic calamitic mesogenic units, all future references relate to this form. Finally, with regard to classification, the mesogenic units may be linked together in a head to tail fashion, forming main chain LC polymers (MCLCP), or they can be appended to a backbone forming side chain LC polymers (SCLCP). This system used to classify liquid crystal polymers is illustrated in Figure 1.6.

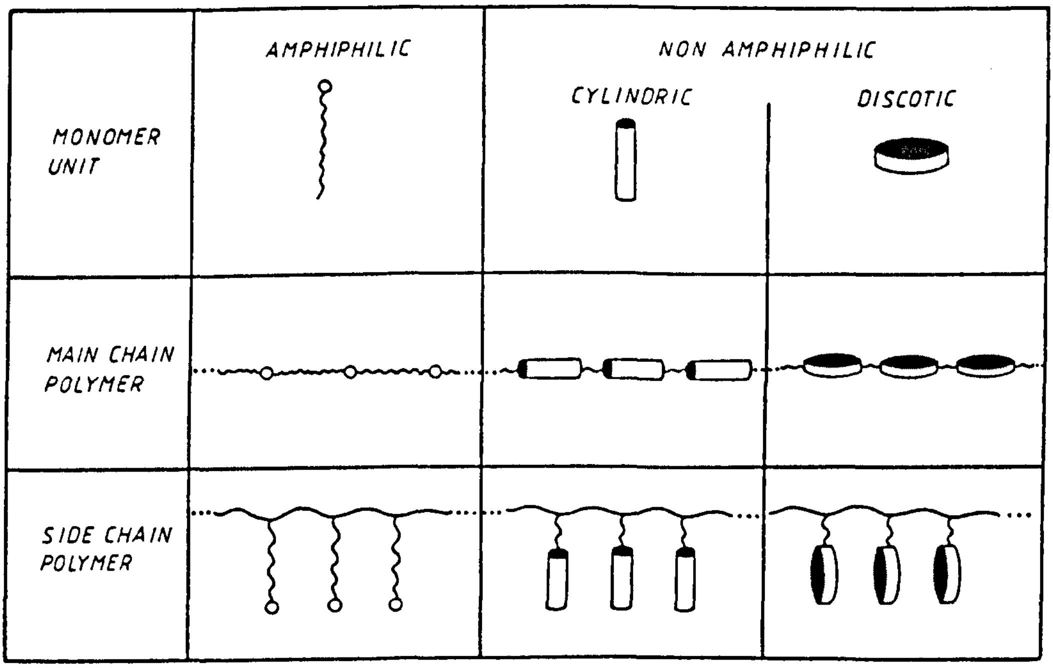


*Figure 1.6*

*Classification of liquid crystalline monomers and polymers*

### 1.2.4 Synthesis

LCP may be synthesised by conventional polymerisation methods. Main chain LCP, for instance, are normally prepared by step-growth reactions such as polycondensation or polyaddition, and these reactions occur between reactants which contain two monofunctional groups. The monomers can either be suitably substituted mesogenic or non-mesogenic compounds which, on polymerisation, form the polymer backbone of the LCP. In this way, polyester and polyamide MCLC polymer systems with high molar mass have been prepared [25].

SCLCP however may also be synthesised by step-growth reactions, but the use of this procedure has been limited in its application, and reports have involved only the synthesis of thermotropic liquid crystal polyesters [26]. More commonly, chain-growth reactions and polymer modification reactions are used to produce SCLCP, and these techniques are discussed in Sections 1.2.4a and b.

### 1.2.4a Chain-growth Reactions

Methacrylate, acrylate and chloroacrylate systems containing mesogenic side chain units are most commonly prepared by free radical polymerisation [27]. Such reactions are usually initiated by α-α'-azoisobutyronitrile, and without appropriate control, generally produce polymers with a range of molecular weights and high polydispersity.
Other synthetic approaches include anionic polymerisation [28], cationic polymerisation [29] and ring-opening polymerisation [30].

In 1983, Webster and co-workers at Du Pont introduced a new method for the anionic polymerisation of esters of methacrylic acid and other α-activated alkenes, a process which was named group-transfer polymerisation (GTP) [31]. The polymers that are formed by this method have narrow molecular weight distributions ($\gamma < 1.3$) and the molecular weights may be controlled. Furthermore, the process produces 'living' polymers, which present the opportunity for reactions involving the functionalisation of the chain end and/or block and graft polymerisation. GTP has been adapted to prepare LC polymethacrylates of low tacticity, moderate polydispersities (1.4 - 1.8) and controlled molecular weights, and these appeared to compare favourably with analogues synthesised by other methods [32].

Some work involving the synthesis of SCLC methacrylates and acrylates by GTP has been performed in these laboratories [33]. Our studies initially involved the polymerisation of methyl methacrylate, with methyl trimethylsilyl dimethylketene acetal as initiator and tetrabutylammonium fluoride as catalyst. This technique was found to be extremely sensitive to moisture and reagents had to be rigorously purified and carefully stored. Our results showed that the properties of the macromolecules depended largely on the ratio of initiator to catalyst, as well as on the ratio of initiator to monomer. However, our attempts to produce SCLC methacrylates and acrylates have met with only limited success, and it has been suggested in the literature that acrylate systems are more difficult to polymerise than the corresponding methacrylate systems [34]. Furthermore anionic polymerisations of acrylates/methacrylates with substituents containing biphenyl moieties have been reported to yield polymers with only low molecular weights [28]. Our results appear to support these general conclusions.

### 1.2.4b Polymer Modification Reactions

This technique involves the transformation of a 'reactive prepolymer' into a SCLCP, by its interaction with terminally functionalised mesogenic molecules to give mesomorphic polymers. The advantage of this method is that critical properties ($\overline{Mw}$, $\overline{Mn}$, $\gamma$) of the preformed polymer backbone have already been established, and hence determine those of the resultant SCLCP. Furthermore, polymer modification reactions allow the preparation of non-classical mesomorphic polymers with new macromolecular backbones, polymers whose synthesis may not be easily achieved by other routes. For example, Keller has recently developed a new procedure for the preparation of SCLCP by grafting mesogenic monomers onto various prepolymers, using phase-transfer catalysed esterification reactions [35]; by these means, Keller has produced the unusual LC polyitaconates, polymaleates and poly(methyl vinyl ether co-maleates), as well as more standard LC polyacrylates and polymethacrylates.

The application of polymer modification reactions is most frequently used in the synthesis of mesomorphic polysiloxanes. Side chain liquid crystal polysiloxanes are prepared by the poly(hydrosilylation) reaction between a preformed polysiloxane backbone with reactive Si-H sites and a mesogenic alkene, in the presence of a platinum catalyst [36]. In order that consistent products are produced, many conditions and procedures have to be adhered to, and these are discussed in Section 2.2.

### 1.2.5 Main Chain Liquid Crystal Polymers

As mentioned earlier, interest in LCP was first reported in the early 1950's and involved the main chain variety [5, 6]. The mesogenic groups, connected head to tail, constitute the monomeric units that actually form the polymer backbone. The mesogenic units can either be rigidly connected together or linked *via* a flexible spacer. In the former case, the melting point of the macromolecule tends to be greater than its decomposition temperature and thermotropic mesophases are not normally obtained. Lyotropic liquid crystalline phases may be observed however, above a specified concentration of an appropriate solvent, which may be concentrated sulphuric acid or a phenol. To form thermotropic mesophases, the rigid main chain must be modified to obtain melting points that are below the decomposition temperature of the polymer. This can be achieved either by the introduction of non-linear, but rigid components in the main chain so that the cylindrical shape of the backbone is broken up, or by the substitution of lateral alkyl chains into the mesogenic groups to act as lubricants between the rod-like particles [37].

Alternatively, the melting point may be lowered by the use of a flexible spacer [38]. A link (consisting, normally, of $(CH_2)_n$ units) may be forged to connect up the more rigid mesogenic groups. This creates a polymer main chain of alternating rigid and flexible segments. With sufficient spacer length, the backbone is transformed into a semi-flexible chain of freely joined rods which have the axial ratio of the original mesogenic unit.

Over the years, research into main chain LCP has led to commercial products, as seen by the development and widespread utility of such materials for applications in the form of fibres, resins and blends. These include 'Kevlar' (Du Pont), a lyotropic LC polyamide (*p*-phenylene terephthalamide [PPTA]); high tensile strength fibres may be drawn from solutions in concentrated sulphuric acid. Main chain liquid crystal polymers are very profitable, since sales of aromatic copolyesters in America command 3% of the high performance polymer market [39]. They are promoted mainly in the electronics industry and supplied, almost exclusively, by three producers -- Amoco with 'Xydar', Hoechst-Celanese with 'Vectra' and Granmont with 'Granlar'.

### 1.2.6 Side Chain Liquid Crystal Polymers

In side chain liquid crystal polymers, unlike the main chain kind, the mesogenic moieties are not integrated into the polymer backbone. Instead, these groups exist as separate entities which radiate from the polymer main chain, to which they are attached, usually *via* flexible spacers. This provision allows for the systematic synthesis of side chain polymers which exhibit thermotropic mesomorphic properties. Work on SCLCP was pioneered both by Ringsdorf and Finkelmann in Mainz [40], and by Shibaev and Pláte in Moscow [41]; their definitive research over the last ten years has led to a good understanding of the subject. Prior to this era, the synthesis of side chain polymers had involved mesogenic units linked directly to the backbone [42]. These materials seldom showed thermotropic mesophases. With the mesogenic groups strongly coupled to the polymer segments, they tended to move in 'unison' with the backbone, and were unable to order anisotropically. As such, either no liquid crystal phases were formed, or at best crystalline polymers with high melting points and a smectic-like structure were obtained.

Ideally, this problem is overcome by the use of flexible spacers which allow partial decoupling of the motions of the mesogenic side chains and the flexible polymer backbone. As independently proposed by de Gennes from theoretical considerations [43], the introduction of spacers results in LCP with enantiotropic mesophase transitions at easily accessible temperatures. This is the basis upon which SCLCP are synthesised today. The model studied experimentally by Finkelmann *et al.* [40] is illustrated schematically in Figure 1.7. It must be stressed that the three polymer 'sections' do not individually dictate that a macromolecular system will be mesomorphic. They act collectively and all three must be taken into account in any attempted prediction of the behaviour of a specific SCLCP.

There are basically two categories of SCLCP, which differ by virtue of whether the rod-like mesogenic groups are attached terminally or laterally to the polymer backbone.

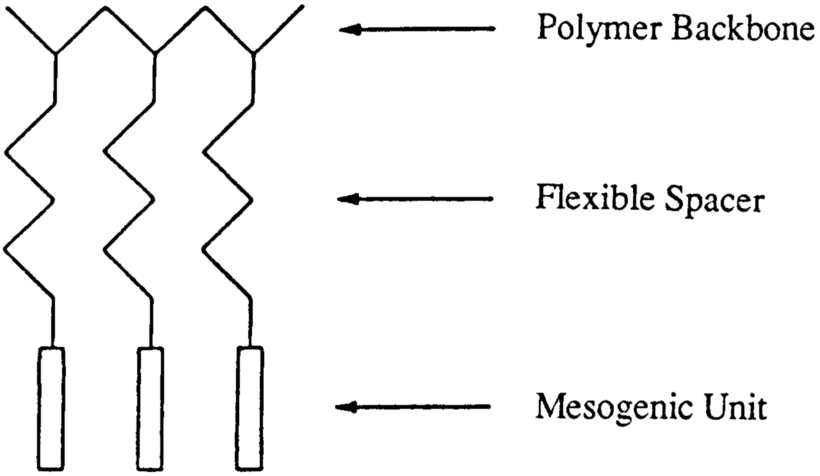


***Figure 1.7***

*Linkage of mesogenic groups to the polymer backbone via flexible spacers*

The early materials prepared were all of the terminally attached or 'comb' type [40]. With increased understanding of the effects of combining mesogenic groups with a flexible polymer backbone, mesogenic side chains were then appended laterally [44]. However, work in this area is still very new, and due to the small number of laterally attached SCLCP currently recorded in the literature, information on SCLCP is derived almost exclusively from results of systematic investigations made on the terminally appended species. Although both forms have characteristics which are unique to that system, various generalisations can still be made based on the original concept proposed by Finkelmann. These are now discussed, and special features relating to laterally attached SCLCP are noted in Section 1.2.7.

### 1.2.6a Polymer Backbone

Many polymer systems have been used to generate SCLCP, but the commonest examples are provided by acrylate and siloxane backbones in conjunction with some classical liquid crystalline moiety attached by its terminus [36, 41]. Finkelmann, in his early work on SCLCP, suggested that the main chain had little or no effect on the anisotropic orientation of the mesogenic side chains, and that the properties of SCLCP were determined by the mesogenic groups alone [40]. However, it has since been shown that the properties of the backbone do in fact influence liquid crystal behaviour [45].

The flexibility of the polymer backbone increases on going from methacrylate to acrylate to siloxane. This property is reflected in the different glass transition temperatures, with the very flexible siloxane backbone giving the lowest Tg value and the more rigid methacrylate backbone giving the highest Tg value. Investigations on the effect of appending the same mesogenic group terminally *via* the same flexible spacer to these three polymer backbones have indicated a similar trend in the mesophase transition temperatures [46]. If the flexible spacer could allow total decoupling of the motions of side chain from polymer backbone, so that the mesogenic groups could align anisotropically and totally independently of any constraints from the polymer backbone, the phase transition temperatures for all three LCP should be the same. The fact that they are markedly different shows that backbone flexibility does have an affect on liquid crystalline properties. Furthermore, the backbone is known to influence the mesophase type [47]. The flexibility of the polymer main chain is able to influence the manner in which the side chains pack, and consequently the type of mesophase formed. With the polysiloxane backbone, the side chains are able to overcome the favoured random coil conformations of the polymer backbone and can align in a lamellar arrangement to give smectic qualities. The more rigid methacrylate backbone however, is not flexible enough to accommodate itself in such a lamellar system (probably in the planes between smectic layers), and is more likely to generate a nematic mesophase.

The constitutional nature of the polymer backbone may be altered by 'diluting' the concentration of mesogenic units with non-mesogenic groups, and these behave like spacers incorporated into the polymer main chain. The interactions between the mesogenic side groups and also between them and the polymer backbone are reduced, and together these effects give lower glass and mesophase transition temperatures [48]. Through the synthesis of such backbone copolymers, LCP may be prepared covering virtually any desired temperature range, thereby producing better materials for potential applications.

The effect of tacticity in the main chains of LCP has been studied by Pláte and Shibaev for some polymethacrylates and polyacrylates [49]. No appreciable difference in mesomorphic properties was observed for the stereoisomers investigated. Blumstein *et al.* also report that tacticity did not appear to have any influence on the packing of the side chains, even though they were for systems with mesogenic groups directly attached to the polymer backbone [50]. This is a surprising result, since glass transition temperatures are strongly influenced by this property -- isotactic polymethacrylate has Tg 45 - 57 °C while its syndiotactic analogue has Tg 115 - 120 °C [28].

However, there have been contrasting results reported for mesogenic polyolefins [51] and polymethacrylates, where LCP with variable tacticities have been shown to display properties that are noticeably different. Optical studies on an anionically prepared isotactic LCP revealed only a smectic mesophase, whereas the syndiotactic species, synthesised by radical catalysis, formed additionally a nematic phase [28]. The nature of the backbone's configuration has however been largely ignored in studies of LCP, mainly because so little work has been carried out to investigate such effects, and these results stress the importance of maintaining an awareness of what may be possible.

Equally, the question arises as to whether there is a correlation between the degree of polymerisation and the transition temperatures of a LCP. Apfel *et al.* suggest that transition temperatures should hardly be affected by molecular weight, as the only ordering that occurs in the liquid crystalline state is an average parallel orientation of the long axes of the mesomorphic side chains, and these are free to cluster regardless of the length of the backbone to which they are attached [52]. Blumstein *et al.* [53], on the other hand, acknowledge that transition temperatures do increase with molecular weight for main chain LCP, and that these reach an almost constant level for $\overline{Mw} > 10\,000$. As monomeric units vary in nature and hence appreciably in molecular weight, this sweeping generalisation is perhaps rather vague and ill defined.

According to Stevens *et al.* [54], the most dramatic differences in transition temperature are observed for oligomers with $\overline{DP} < 10$. Furthermore, they found that only slight variations occurred within the $\overline{DP}$ range 10 - 100, and that there was a seemingly complete independence of $\overline{DP}$ for systems where $\overline{DP} > 100$. This claim is seemingly supported to a certain extent by work performed on ferroelectric LCP [23] which showed that increases in transition temperature were no longer significant after $\overline{DP} > 30$. However, it has since been established that these assertions are not true, and that distinct variations in transition temperature can occur even up to $\overline{DP}$ 100 and beyond [55]. In addition, fluctuations in the polydispersity of the polymer cause similar variations.

### 1.2.6b The Flexible Spacer

A mesogenic side chain linked directly to the polymer backbone would be expected to be severely curtailed in its freedom to move and align anisotropically by the main chain's attempts to adopt the energetically favoured random coil arrangement. The flexible spacer operates on the principle that it distances the mesogenic group from the total domination of the backbone. This allows for partial decoupling, and weakens the mutual motional influence of main chain and mesogen. In doing so, the mesogenic groups are able to align anisotropically and form thermotropic mesophases.

The effects of length of the flexible spacer, expressed as the number of atoms connecting mesogenic unit to polymer backbone, have been much investigated [56, 57]. The thermal stability and type of mesophase depend critically on this length. When too short, the mobility of the side chains is constrained, since the spacer then effectively behaves as a direct link between the pendent group and the backbone, and only isotropic polymer melts have been obtained [58]. Conversely, if too long a spacer is introduced, side chain crystallisation has been observed to take place preferentially [59]. The use of a very long spacer therefore leads to closer interactions between mesogenic groups and adoption of crystalline ordering. Layered ordering is possible with somewhat shorter spacers, and smectic phases are normally observed [60]. The number of atoms judged to be best is between 5 and 8, as this allows for sufficient decoupling, in order that liquid crystalline polymers with glass transitions are obtained. If nematic properties are possible for a particular mesogenic group and backbone, these will occur with the shorter spacers.

Glass transition temperatures are observed to fall with increasing length of spacer. With less conformational strain imposed on the main chain by the mesogenic units, the flexibility of the system increases proportionately, and is reflected in the reduced Tg values [46].

Odd-even alternation effects on phase transition temperatures, first observed for LMM LC materials [61], have also been reported for SCLCP and relate to the number of connecting atoms in the spacer [56].

The flexible spacer must not therefore be thought of as just a means of connecting the mesogenic unit to the polymer backbone, i.e., it is not 'inert'. In fact, it has been found that changes in the chemical constitution of the flexible spacer can have a profound influence on the properties of the SCLCP [62]. The most commonly used spacer is that consisting of chains of methylene groups or polymethylene chains that also include an ether function. Polymers with spacers containing glycol type units $[O(CH_2)_nO]$ only form mesophases if the monomers do, and these phases are of the same type.
The phases are however, stabilised on polymerisation. This has led to the proposal that these more flexible spacers are (a) highly efficient at decoupling polymer main chain and mesogen, so that the mesomorphic behaviour of the polymers is like that of the monomer, but (b) generate higher transition temperatures by increasing order in the system. Attempts to incorporate the even more flexible siloxane unit in a spacer have proved to be complex, since the very bulky siloxane group disrupts liquid crystalline order. However, the degree of decoupling is thought to be even further improved. Polymers have also been synthesised with spacers containing an ester group [63] and a carbonate group [64].

Although it is generally accepted that a sufficiently long spacer is able to decouple the motions of main chain from mesogenic group, studies have shown that this decoupling is not total. ESR spectroscopy (angular dependent spin-probe studies) indicates that dynamic coupling of the backbone and side chain motions does occur *via* the spacer [65]. This accounts for the high viscosity of SCLCP and the fact that their electro-optic response times are at least one order of magnitude larger than those for their LMM analogues, even when long spacers are used. Furthermore, $^2H$ NMR measurements on selectively deuteriated polymers have revealed that sections of the spacer can take part in the anisotropic orientations of the mesogens [66]. Macroscopic alignment in electric and magnetic fields, on the other hand, depends very much on spacer length and molecular weight. As such, the use of sufficiently long spacers can give rise to polymers with threshold voltages and elastic constants that are comparable to low molecular weight liquid crystals [67], even though response times are slow.

### 1.2.6c The Mesogenic Unit

For a molecular unit to 'qualify' as a side chain precursor, it must first have a structure compatible with mesophase formation, i.e., it must be mesogenic, and conform with structure-property relations for LMM systems that have already been well documented [68]. Only then can the moiety impart the qualities of liquid crystallinity, in combination with the mechanical strength of polymers, characteristics that are inherent in LCP. Up to now, this association of side chain and backbone in terminally and some laterally attached SCLCP has brought about enhanced thermodynamic properties, such as increased glass and phase transition temperatures and higher orders of mesophase [46]. The strong influence of the bulky side chains, which stiffen and hinder the mobility of the main chain segments, explain the higher Tg values of the SCLCP compared with the unsubstituted backbone. Furthermore, the order of the mesogenic groups is promoted upon its linkage to the polymer backbone, as reflected by the increased mesomorphic properties.

The mesogenic side chains may either be rod-like (calamitic) or disc-like (discotic) in shape. The disc-shaped units contain rigid, usually aromatic cores such as triphenylene with generally unbranched alkyl chains. Structural modifications have enabled the synthesis of polymers carrying disc-like mesogens either as side groups [69] or within the polymer main chain [70]. These exhibit discotic phases, which are quite distinct from those normally observed for calamitic systems. As the work for this thesis concentrated on the use of rod-like mesogenic units, all further references to side chains relate only to these systems.

The relationships between molecular structure and liquid crystalline behaviour for low molar mass systems have been extensively investigated [10, 61]. A detailed account is beyond the scope of this thesis and only some general points are mentioned here. Since the majority of this work has involved the synthesis of materials which exhibit the nematic phase, the effects to be discussed deal exclusively with this phase type.

For a low mass molecule to form a mesophase, the core of the molecule has to be fairly rigid and elongated, i.e., have a high length-breadth ratio. Over and above this, the core often carries polar groups that are capable of increasing the anisotropy of molecular polarisability ($\Delta\alpha$). With this in mind, it can be seen that an extension to the long molecular axis of the rigid core structure generally raises the nematic thermal stability, so long as the terminal substituent does not significantly broaden the molecule. Non-polar, terminal alkyl groups are also frequent features of the molecular structure of mesogens. Although they do not have a strong effect in enhancing nematic thermal stability, they are important in increasing the prospects of obtaining low melting materials. A branched alkyl chain would of course decrease liquid crystal thermal stability relative to that of an open chain alkyl compound [71]. This effect is found to be more significant when the branching occurs close to the mesogenic core. As such, any terminal substituent that is not too bulky is superior to hydrogen in terms of promoting nematic thermal stability, and this property is increased if the substituent is able to extend the conjugation of the core unit. Generally, it is expected that the greatest advantages are obtained from substituents that are compact, polar and polarisable. An average terminal group efficiency order, which has been established for the nematic phase is [10]:

$Ph > NHCOCH_3 > CN > OCH_3 > NO_2 > Cl > Br > N(CH_3)_2 > CH_3 > F > H$

In the case where the terminal substituent is an alkyl or alkoxy group, homologous series of low molar mass mesogens show regular trends of alternation in nematic to isotropic phase transition temperatures on progressing through the series [61]. When considering the number of carbon atoms in the alkyl chain, the odd members have higher N - I transition temperatures than the even members. With alkoxy derivatives, the oxygen is equivalent to a $CH_2$ group, and so the reverse situation is obtained. This pattern of alternation, where the N - I temperature of one set of members forms a curve higher than the other, is always maintained, although its shape depends on the molecular structure. As such, the curves either rise or fall, and the same trend may occur for both odd and even members, or for one or the other. However, this alternation effect always becomes less pronounced as the homologous series is ascended.

The introduction of a lateral substituent broadens the core of the mesogen, increases the separation of the molecular long axes, and generally leads to a reduction in the thermal stability of the phase; in the case of nematics, the effect is in proportion to the size of the substituent. A large substituent may cause the molecule to deviate too strongly from being rod-like and prevent mesophase formation [72]. Associated factors are steric and electronic effects; a steric effect, which causes deviations from molecular planarity, depresses transition temperatures even further [73], while different electronic effects contribute differently to the polarisability across the long axis, thereby affecting the anisotropy of the molecular polarisability. It is also observed that a given lateral substituent decreases the N - I temperature more if the molecule is short [74], presumably because the anisotropy of molecular polarisability is proportionately more affected.

As the structure of the mesogenic unit 'controls' the thermal attributes of the resultant SCLCP, specific phase transition temperatures may be obtained by careful side chain selection. Indeed, in many cases, the effects of the structure of the mesogenic units on the mesomorphic properties of SCLCP are analogous to those established for LMM and exemplified in the text above [75, 76]. Some further examples are:

(i) Increasing the length of a terminal chain (alkyl/alkoxy) promotes smectic tendencies, but reduces glass transition temperatures.

(ii) Incorporating strongly polar end-groups leads to smectic phases, with increased glass transition and clearing temperatures, although the extent to which this occurs depends upon the polarity of the terminal group.

(iii) Changing the chemical structure of the central core, by reversing the ester link between two phenyl rings for example, may result in a change in mesomorphic behaviour. For example, a transformation from a smectic A to a nematic material may be obtained.

(iv) Replacing an ester link in the central core with a more flexible ether link causes a fall in transition temperature, to the extent that the mesomorphic character may be totally extinguished.

It is apparent therefore that the making of subtle alterations in the chemical constitution of mesogenic side chains can have marked effects on the mesomorphic and physical properties of SCLCP. The existence of a smectic C phase, for instance, provides the opportunity of preparing ferroelectric SCLCP, and may sometimes be achieved simply by replacing a non-chiral terminal tail group with a chiral one.

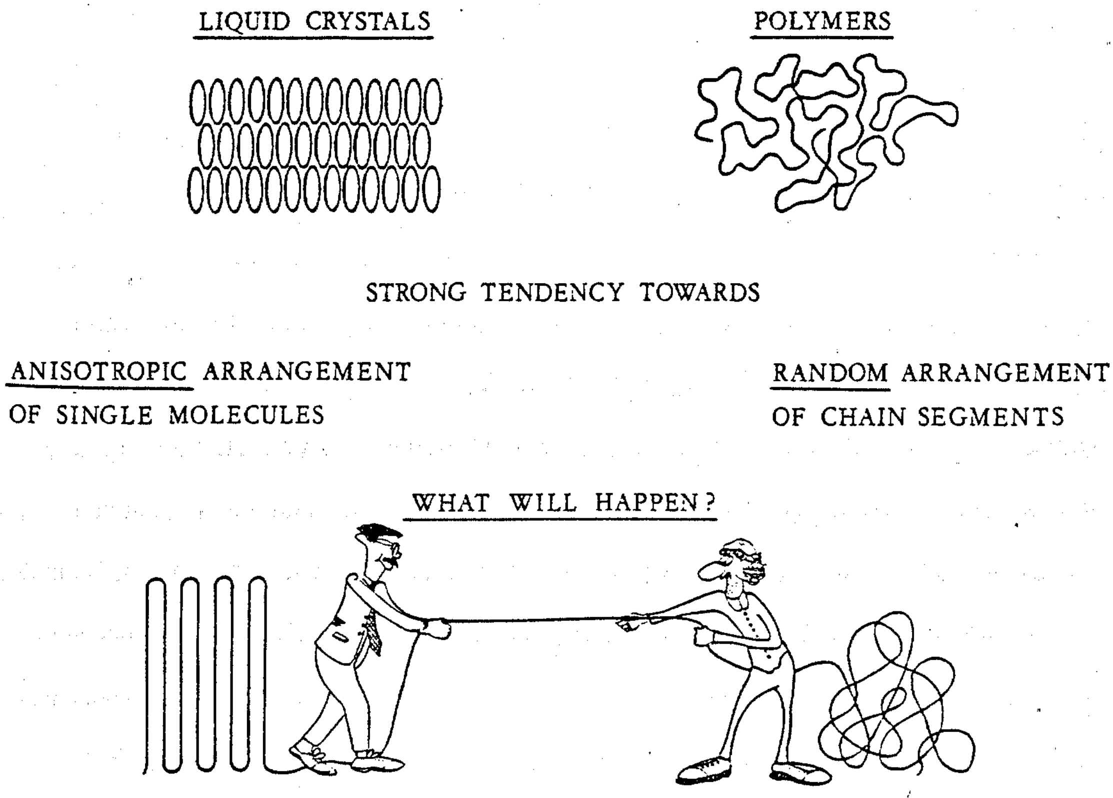
Another method by which the properties of SCLCP can be controlled is by copolymerisation, incorporating appropriate proportions of either non-mesogenic units [48] (to give backbone copolymers, see Section 1.2.6a) or of different mesogenic groups [56] (to give side chain copolymers) in the polymer. In this way, the characteristics bestowed upon the LCP by the dominant mesogenic moiety -- viscosity, phase types, glass and phase transition temperatures, birefringence and dielectric properties -- are 'diluted' by the presence of the other, in order that the properties of the final polymer may be fine tuned.

### 1.2.6d The Model

After having had an in-depth look at the three components that constitute thermotropic SCLCP, it is perhaps useful at this point to review some of the general considerations involved. It must be remembered that a conflicting situation exists (Figure 1.8), with the polymer backbone tending towards a random arrangement of chain segments and the mesogenic groups, on the other hand, endeavouring to take up an anisotropic orientation. Depending on the molecular structure, one factor may dominate over the other.

*Figure 1.8*

*Representation of the conflict between liquid crystalline and polymer tendencies*



The problem was resolved by the conception of the flexible spacer unit. This non-rigid linkage effectively acts as a buffer between the two merged entities, and offers a compromise to the two otherwise extreme configurations of the backbone and side chain respectively. The flexible spacer is able to liberate partially the motions of main and side chain. This allows the components to follow their preferred orientational tendencies, and the statistical distribution of backbone conformations do not prevent the side chains from adopting their anisotropic arrangement. The polymer is now likely to form an enantiotropic mesophase.

However, it must be stressed that this decoupling is not complete. By the very existence of a linkage, a somewhat mutually dependent situation must exist, and the steric interactions of the bulky, aligned mesogenic groups must influence the conformations of the main chain, while the constraints of the backbone must restrain the free anisotropic motions of the mesogenic groups [40]. However, it is the ability of the mesogenic units to adopt anisotropic orientations, in opposition to any forces imposed by the backbone, that enables the occurrence of mesophases in side chain polymers.

Since the polymer backbone has some control over the free translational and rotational motions of the side chains, by virtue of their attachment to the main chain, this imposes some characteristics on SCLCP which are not observed for low molar mass mesogens. The increased order in the polymers gives rise to higher transition temperatures and more ordered mesophase types on moving from monomer to polymer [46]. For example, non-LC monomers may give nematic polymers and nematic/cholesteric monomers may produce polymers which show smectic phases. The mesomorphic properties, however, depend on the interactions of the three component parts and their molecular structures. These various factors have already been discussed in Sections 1.2.6a - c, but are summarised here:

1. Polymer Backbone
   (i) Flexibility
   (ii) Tacticity
   (iii) Molecular Weight
2. Flexible Spacer
   (i) Length
   (ii) Chemical Nature
3. Mesogenic Unit (Side Chain)
   (i) Shape
   (ii) Terminal and Lateral Substituents
   (iii) Polarisability
   (iv) Copolymerisation

### 1.2.7 Laterally Attached Side Chain Polymers

A new class of liquid crystal side chain polymer, with mesogenic groups laterally attached to the main chain through flexible spacers, has been synthesised recently. This macromolecular system was first conceived by Hessel and Finkelmann, and the polymers prepared were of the polyacrylate type (Figure 1.9) [44]. Further reports have involved the synthesis of polymethacrylates [77] and polysiloxanes [78], with side chains based on a similar molecular core structure. The mesogenic units and the attached flexible spacer used are structurally analogous to low molar mass nematic materials prepared by Weissflog *et al.* [74]; these consisted of mesogenic groups laterally substituted with long aliphatic alkyl chains. At first, these observations by Weissflog appeared to contradict the established rule that only relatively small lateral substituents may be used, since low mass molecules that exhibit liquid crystallinity have to be essentially rod-like [72]. Later it was realised that the flexible lateral chains may bend sufficiently to lie parallel to the core structure which was one consisting of three *para*-phenylene groups with ester central linkages, a structure known to give highly thermally stable mesophases [79]. The long lateral substituents also discouraged smectic layering and the materials were predominantly nematic.

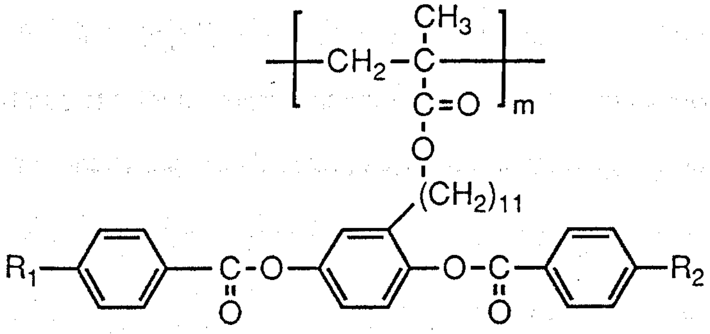


***Figure 1.9***

*First reported synthesis of a laterally attached side chain liquid crystal polymer*

Zhou *et al.* have proposed the term 'mesogen-jacketed polymer' to describe the laterally attached SCLC polyacrylates they have synthesised [77]. Their results are unusual, for they elected to discard convention, by preparing polymers of the laterally attached kind with short linkages. As such, the flexible spacer concept required in conventional SCLCP to decouple the mutual motions of main and side chain appears not to be necessary. It is interesting to note here that the monomers are non-liquid crystalline, but the polymers show stable mesophases with broad nematic ranges. It would appear that the increased mesogenicity on passing from monomer to polymer is similar to that established for terminally attached SCLCP [46]. The overall explanation offered by the authors is that by having the linkage point between mesogenic unit and main chain strategically located at the gravity centre of the mesogen, and by using quite short spacers (one $CH_2$ unit), the main chain is able to encourage mesophase formation by drawing the mesogenic units closer together and constraining them into alignment. They have substantiated these results, by using the same monomeric system to synthesise a liquid crystal polymethacrylate [80].

The results of Keller *et al.* have been of particular interest [78]. Their work on polysiloxanes showed that the polymers have nematic to isotropic transition temperatures that are just 4 - 6 °C higher than those of the mesogenic side chains, and in one case, the polymer had a value that was 1 °C lower. The stability of the mesophase is therefore only weakly improved on passing from monomer to polymer. Although the increases in thermal stability for the lateral systems have been likened to those that occur for terminally attached SCLCP, all the literature results to date have shown that the magnitude of the effect is not as great as with the usual comb-like polymers [46]. More examples of polysiloxanes with laterally attached side chains have been made in this work and consistently, if unusually, show decreases in mesogenicity from monomer to polymer [81, 82]. Attempts to explain this behaviour are given in the Results and Discussion chapter of this thesis.

Another interesting property of the polymers prepared in this work is that they exhibit only nematic phases, even when terminal polar groups, long terminal alkyl chains or long spacers have been used; terminally attached analogues of the polymers have tended to be smectic in nature. Nematic properties predominated too for the limited range of laterally attached SCLCP prepared by others, prior to the present research, and it was suggested that the lateral mesogenic groups form a 'sheath' around the polymer backbone [77]. The mesogenic groups do not then readily form smectic layers.

In addition, since the rotational motions of the mesogenic units around their molecular long axes are restricted, as a result of appending each side chain laterally from a point along its perimeter, the occurrence of a biaxial nematic state might be anticipated. Few low molar mass liquid crystals have shown this phenomenon, but by macroscopic homeotropic alignment of the mesogenic groups, followed by conoscopic observations, Hessel and Finkelmann have been able to obtain interference patterns, which appear to substantiate optical biaxiality in the nematic phase of a laterally attached SCLCP [83].

### 1.2.8 Miscellaneous

There have been many publications and books on SCLCP since their discovery [84, 85], and apart from the conventional kinds discussed so far, there have been reports of variations to these classes. Such 'hybrid' occurrences may be rare, but are nevertheless interesting, for they offer new possibilities and alternatives to what would otherwise be a more limited field of opportunities. Furthermore, these systems help in the understanding of structure-property relationships in macromolecules.

Thermotropic LCP have been obtained largely by incorporating rigid, rod-like or disc-like molecules as side groups or as part of the main chain of macromolecules. Terminally attached SCLCP have also been synthesised with structurally varied mesogenic units, e.g., having paired mesogens [62] or swallow tailed mesogens [86]. Reck *et al.* have successfully prepared liquid crystalline polymalonates with mesogens both in the main chain and as side groups [26]. The inclusion of mesogenic side groups in the polymer main chain did not appear to disrupt the mesomorphic properties, and it is assumed that there is in fact, a strong tendency for the side chains to arrange themselves parallel to the mesogenic moieties in the main chain. This constructive interaction of both types of mesogenic group is probably responsible for the observed enhanced mesophase stability.

Work on novel siloxane side chain copolymers with both terminally and laterally attached mesogenic pendent groups has been pioneered in these laboratories [87, 88]. From these studies, it has been found that by varying the type and ratio of the respective side chains, it is possible to control both the thermal and mesomorphic properties of conventional siloxane polymers. The introduction of only small amounts of the lateral side chain component into a predominantly terminally substituted SCLCP has very striking effects, to the extent that smectic phases are totally suppressed and the polymers exhibit nematic phases only. The effects are very small in the reversed situation. These systems have been further investigated in the current research and are reported in Section 4.4.

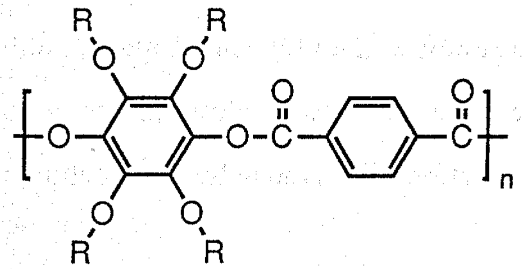
If a linear polymer is chemically cross-linked by a suitable agent, the backbones are no longer able to glide past each other above the glass transition temperature. The viscous linear polymer is thus converted into a form-retaining material. As the chain segments are still mobile, the polymer network may be regarded as an elastic liquid. If mesogenic groups are fixed to the chain segments, an elastic, form-retaining liquid crystalline polymer is obtained, with similar properties to those of the linear polymers [89].
The influence of cross-linking depresses both glass and phase transition temperatures, but the same phase type is maintained. In this way, LC rubbers exhibiting any required phase type can be synthesised; these exhibit the elastic properties typical for conventional cross-linked polymers, as well as the liquid crystalline properties.

The synthesis of liquid crystalline polymers is not, however, restricted to long chain macromolecules, which may be either linear, branched or cross-linked into networks. Recently, cyclic poly(hydrogenmethylsiloxane) fractions have been obtained and interacted with suitable mesogenic alkenes to form LC cyclic polymers [90]. In a comparative study of cyclic siloxanes with their linear analogues, the smectic-isotropic transition temperatures of the cyclic materials are found to be generally higher relative to the linear materials, and this may be partly attributed to the absence of trimethylsilyl end-groups in the cyclic systems [91]. Such end-groups would be expected to dilute the mesophase, thereby lowering the transition temperatures of the linear polymers.

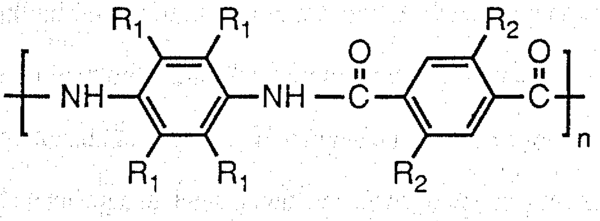
As it was, phase textures similar or identical to those obtained from LMM liquid crystals have been identified for LC cyclic siloxanes (smectic A, B, E, nematic, cholesteric) [92]. The transition temperatures do not appear to show any trend with increasing ring size, contrary to the effect of rising transition temperature with increasing molecular weight observed for the linear derivatives [54]. Attempts have also been made to determine, by conoscopic studies, the type of phase exhibited by LC cyclic polymers, i.e., whether the phase types are calamitic or discotic in character [92]. The conclusions reached are that the nematic and smectic phases of the cyclic materials are calamitic, while the cholesteric materials have a discotic structure. Furthermore, the possible conformations of LC cyclic siloxanes have been predicted by computer simulations. Instead of existing as a simple planar structure, they are believed to be arranged in a paired or interdigitated manner; this concept is supported by x-ray measurements.

There has been a recent announcement of a new class of mesophase called the sanidic mesophase, and this has also been displayed by highly substituted rigid-rod polyesters and polyamides [93]. The shape of the molecule or mesogenic unit, which is assumed to be responsible for the mesophase formation, is board-like (Figure 1.10). These molecules have been observed to stack on top of each other in either an ordered or a disordered way, with the stacks of molecules orientated parallel to each other.

Polymorphism exists through the possibility of different ordering within the stacks, as well as in the spatial arrangements of the stacks. X-ray scattering investigations show that the structures of these mesophases differ from those observed for conventional discotic and calamitic systems.



(a)



(b)

*Figure 1.10*

*Chemical structures of 'board-like' units which display sanidic mesophases when incorporated as repeat units in*
*(a) polyesters or*
*(b) polyamides*

## 1.3 PHYSICAL PROPERTIES

The widespread occurrence of low molar mass liquid crystal materials in every day applications can be attributed to the advances that have been made in understanding the relationships that link the physical and the chemical properties. From the brilliant concept of the basic twisted nematic device [94], progress in application development has come about largely through the clear interpretation of the physical properties associated with mesogenic molecules. Parameters could then be fine tuned, to allow the physics of liquid crystals to respond to device demands.

As correlations between the physical properties and the molecular structure were identified, it became clear that the chemistry could be integrated with the physical requirements, and the demands of the device engineers and physicists could be met by the materials scientists. However as is often the case, compromises have to be accepted in designing the 'best' structure or mixture to give optimium performance in a given application. Testimony to these efforts is given by the sophisticated, state-of-the-art LC devices available today.

As the majority of applications rely on the nematic mesophase, the physical parameters now discussed, unless specified otherwise, relate to this phase type.

### 1.3.1 Order Parameter

The order parameter, S, describes the ordering of the molecular long axes with respect to the nematic director, (**n**). This is a measure of the efficiency with which the molecules in the mesophase align parallel to the director, and is described by the equation:

$S = {}^1/_2 < 3\cos^2\theta - 1 >$

where $\theta$ represents the angle between the director and the molecular long axis of the mesogen. The molecules which line up in a nematic phase are not fixed in their position, but tend to oscillate about the director due to thermal motion. As such, a space-time average is required to take this into account mathematically, and this is represented by the angled brackets (< >). The values for the order parameter S, which are dimensionless, range from 0 for the isotropic liquid to 1 for cases where the molecules are all exactly parallel to the director -- nematics have values from 0.4 to 0.7. The higher the value of S, the more perfectly the molecules are aligned with the director, i.e., the mesophase is more anisotropic. The order parameter is temperature dependent and increases with falling temperature. As such, there is a need to quote the temperature at which any physical measurement is made, together with the value for the order parameter.

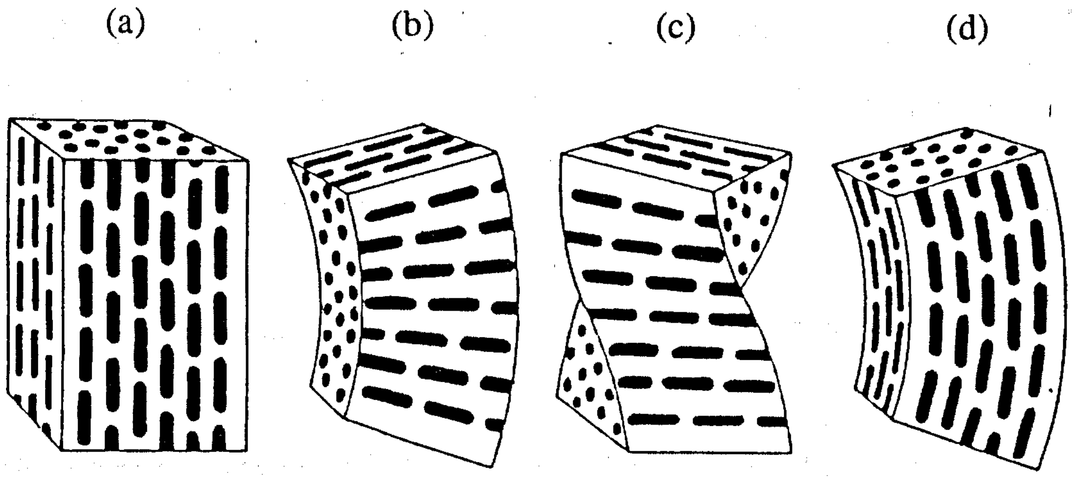
### 1.3.2 Elastic Constants

In the nematic phase, as stated above, the molecules orientate themselves in a preferred direction with respect to the director (**n**). Any distortion of the undisturbed state requires energy, because, in a mesophase, an elastic torque exists which tries to maintain the original configuration. However, even in the absence of external forces, boundary conditions can effect configurational deformations.

There are three types of elastic deformations. These are known as splay, twist and bend and are represented by the constants $k_{11}$, $k_{22}$ and $k_{33}$ respectively (Figure 1.11). On experiencing a deformation, a nematic system will therefore attempt to restore the original molecular order, and the elastic constants relate to the energy that resists control by a particular type of deformation. Without involving mathematical expressions and equations, about which greater detail on the subject may be obtained from appropriate publications [95], it suffices to say that a low ratio for $k_{33}$ to $k_{11}$ is preferred, since this enables good device threshold sharpness and multiplexing addressing. The elastic constants are temperature dependent, and decrease as the temperature increases, but the ratios, such as $k_{33}:k_{11}$, are mainly independent of temperature.

*Figure 1.11*

*An ordered liquid crystal is given in (a) its equilibrium configuration. The deformation states required in order to adequately describe all possible deformation patterns are (b) splay, (c) twist and (d) bend.*



### 1.3.3 Birefringence

As an incident light ray passes through a liquid crystal medium, the beam is split into two components, the extraordinary ray (e-wave) and the ordinary ray (o-wave), which are polarised at right angles to each other and travel at different velocities. This optical property, known as double refraction, is related to the anisotropic nature of liquid crystal materials. The e- and o- waves that emerge have different velocities, and these lead to the refractive indices $n_e$ and $n_o$ respectively. Alternatively, they may be assigned as $n_{||}$ and $n_{\perp}$, and represent the refractive indices either parallel or perpendicular to the nematic director. The birefringence, $\Delta n$, of a liquid crystal can then be defined as the difference in refractive indices between that of the extraordinary and the ordinary rays, i.e.,

$$\Delta n = n_e - n_o$$

or $\Delta n = n_{||} - n_{\perp}$

In nematic and smectic liquid crystals, the director (**n**) is parallel to the optical axis. This gives a value for $n_e$ that is larger than $n_o$, and the difference of $\Delta n$ is always positive. With the cholesteric phase however, the helical structure is orientated such that the molecular director is perpendicular to the optical axis. The velocities of the two rays are almost equal, but the value for $n_o$ is generally slightly larger than $n_e$. This results in $\Delta n$ being negative. Liquid crystalline materials are thus available either with high (0.1 to 0.3) or low (< 0.1) values of birefringence.

### 1.3.4 Dielectric Anisotropy

The dielectric anisotropy, $\Delta\varepsilon$, of liquid crystals is defined as the difference between the dielectric permittivities measured parallel ($\varepsilon_{||}$) and perpendicular ($\varepsilon_{\perp}$) to the director (**n**), i.e.,

$$\Delta e = \varepsilon_{||} - \varepsilon_{\perp}$$

Due to the dielectric anisotropy of the nematic phase, the director tends to orientate itself in an electric field. If $\Delta\varepsilon$ is positive, the director aligns in the direction of the field, but does so perpendicular to the field if $\Delta\varepsilon$ is negative. The sign and magnitude of the dielectric anisotropy is dependent on the orientation and strength of any dipole moments, permanent or induced, relative to the molecular long axis. $\Delta\varepsilon$ values are temperature dependent, which means that there is a need to quote the temperature at which the measurements are made. $\Delta\varepsilon$ is also an extremely important parameter for most devices and applications.

It is known that mesogenic moieties with terminal polar groups (e.g., cyano) have high positive dielectric anisotropies, since the dipole moment acts along the molecular long axis. However, it has been shown by x-ray diffraction and neutron scattering studies that the terminal cyano-substituent in a mesogen gives rise to a phenomenon known as 'antiparallel correlation', otherwise more correctly referred to as 'antiferroelectric short-range ordering' [96]. Instead of existing as discrete molecules, dipole-dipole interactions cause the molecules to exist as loose, antiparallel pairs or dimers. Due to the partial overlap of molecules, the effective overall length of the dimer is generally about 1.4 x the molecular length. The consequence of this molecular pairing is a reduction in the contribution of the cyano- dipole moment to $\varepsilon_{||}$, and hence $\Delta\varepsilon$, since the dipoles are effectively cancelling each other out. To destroy antiparallel correlations, small amounts of non-polar mesogens are normally added. These molecules split up the dipole associations, and allow maximisation of the dielectric properties by increasing the contribution from the dipole moment of the polar group parallel to the molecular long axis [97].

### 1.3.5 Viscosity

As in the case of all the other physical properties, viscosity is anisotropic; it is however a complex property and can only be defined rigidly by six viscosity coefficients, represented by $\alpha_1$ to $\alpha_6$. A macroscopic viscosity may however be determined by capillary flow or rotating cone methods, and is strongly affected by temperature. This is a most useful parameter and it is found that low molar mass LC materials of low viscosity are best for most opto-electronic applications, since faster response times are observed for materials that are less viscous. LCP are of course greatly more viscous than low molar mass LC [98], but again it can be assumed that if the viscosity of polymers can be minimised, they are more likely to find applications, in some areas at least.

## 1.4 APPLICATIONS

The commercial significance of liquid crystals cannot be emphasized enough. Since the discovery of the 4-n-alkyl- and 4-n-alkoxy-4'-cyanobiphenyls in 1972 by Gray and Harrison [99], nematic, cholesteric and smectic liquid crystals have been successfully used in a variety of technological applications. This has been especially the case with nematic liquid crystals for electro-optical display devices; their use is now widespread in many forms of visual displays.

It became apparent very early on that SCLCP could not really compete in the same technological area as their LMM analogues. Although the materials exhibit a range of electro-optical effects, the high bulk viscosities of these systems infer that the response times of LCP will be too high for use in fast switching display devices. This has been confirmed practically [98], although recent reports of fast switching (1 - 2.7 ms when driven by a d.c. field of 40V) for some ferroelectric smectic C LCP suggest that sweeping generalisations on this issue may be dangerous [22].

The existence of glass transitions in LCP necessitates that operating temperatures in any device are in excess of Tg, but this is no different to the problem of melting point for LMMLC.

Despite the viscosity problem, SCLCP do have the potential to fill a void in the commercial market, through their use in different, as well as in complementary applications to those of their monomeric counterparts.

Liquid crystal polymers combine the viscoelastic properties associated with polymers, with the electro-optical properties characteristic of low molar mass liquid crystals. This combination opens up the possibility of new display devices with novel fabrication techniques. Currently, most displays require a thin, sealed, sandwich-type cell to hold the liquid crystalline material. This could be replaced by thin films or coatings of polymer liquid crystals, thereby simplifying the constructional requirements of the devices. Furthermore, the potential applications could be geared towards exploiting the specific qualities of polymeric materials, namely their mechanical strength and the unique property of the glass transition. In the presence of an applied field or external influence, the induction of order (or disorder) in the system, either in the form of a change in the absorption, birefringence or scattering properties of the LCP, would constitute the input of information which could then be 'locked in' and stored, when the sample is cooled rapidly to below the glass transition temperature. With this in mind, applications can clearly be envisaged in the form of optical data storage systems.

An alternative approach is for the use of materials with Tg below ambient temperatures, and simply to have the information stored in the enormously viscous smectic phase of the SCLCP. This has been demonstrated for a smectic polysiloxane, with electro-optical effects induced both by an electric field and by laser addressing [100, 101]. The information input with an electric field was best carried out just below the clearing temperature, where response times are faster. With laser addressing, the application of a computer controlled laser beam creates an optically visible texture change, usually by heating the polymer locally such that the isotropic liquid is obtained.. Using a combination of laser addressing and applied fields, both writing and selective erasure are achieved. The contrast in such storage devices may be accentuated by the guest-host effect. By copolymerisation, some of the side chains have the property of dyes. The dye groups move in a co-operative fashion with the mesogenic side groups, giving enhanced changes in absorbance. They do not therefore disrupt the mesomorphic properties, and furthermore, the presence of the dye is found not to affect switching times. This is an advantage over monomeric liquid crystals, where the inclusion of dye molecules causes a marked increase in electro-optic switching speeds. The dye may also be introduced by simply dissolving it in the polymer matrix. The advantage of LCP over low molar mass materials as storage media is that the smectic phases of such polymers are very highly viscous and have high thermal stabilities. As such, they are capable of storing data without the dangers of corruption by mechanical stress, and are able to do so over a large thermal range.

The viscoelastic properties of SCLCP may also be used to modify the behaviour of low molar mass liquid crystals [100]. Through their use as dopants, the addition of such LC polymers has been found to give improved multiplexing capability and performance, without drastically affecting response times.

Another well developed application involving thermotropic SCLCP relates to their use as stationary phases for gas chromatography (GC). Conventional GC solvents rely on separations based on solute vapour pressure and/or differential solubility arising from specific energetic interactions. Nematic stationary phases, however, give separations based upon differences in solute molecular shape, or in the instance of cholesteric phases, solute chirality. These mesomorphic stationary phases thus provide selectivity on an entirely different basis from that of all other GC stationary phases. Their use has enabled enhanced separations of many isomeric species to be achieved, e.g., separations of polycyclic aromatic hydrocarbons which have been difficult or even impossible to bring about by other traditional chromatographic techniques [52, 102]. Studies have also been conducted using chiral siloxanes for use in supercritical fluid chromatography [103].

Pláte and Shibaev first suggested the use of cholesteric SCLCP as selective light reflectors or filters [104]. A cholesteric polymer, reflecting a specific wavelength of light at a temperature above ambient, may be quenched below its Tg. As the helical pitch is not altered, the optical properties are frozen in the glassy matrix. Furthermore, these polymeric films display the polarising properties of cholesterics, thereby allowing them to be utilised as circularly dichroic optical films.

Finkelmann, in a recent review, has reported a useful feature of liquid crystal elastomers [105]. The deformation of a macroscopically aligned film in the liquid crystal state causes local changes in the director and in the optical properties. A 'stamp', which may have defined patterns of micron dimensions, can then be used to create these local deformations of the optical axis. This enables light conducting pathways to be pressed into the elastomeric film and durably stored in the glassy state, so affording a relatively simple method of producing elements for integrated optics.

LC elastomers, with their property of high optical transparency, are also considered interesting materials for non-linear and integrated optical applications [106]. Organic materials, containing electron donating and electron withdrawing groups both connected by a conjugated system and forming non-centrosymmetric crystals, can display pronounced second order non-linear optical (NLO) effects. A SCLC polymeric network, into which is locked a non-centrosymmetric arrangement of suitably structured side chains, may offer improved physical and mechanical properties, in addition to the potential for enhanced alignment through poling the polymer as it cools from the isotropic or mesomorphic state [107]. The result of such a fabrication technique may afford materials with a more efficient NLO response [108]. Alternatively, thermotropic nematic LC copolymers, doped with molecules with large molecular hyperpolarisabilities, have been shown to give large second order NLO coefficients through guest-host interactions [109].

Finally, polymer dispersed liquid crystals (PDLC) have recently emerged as a new class of display device [110]. They are included in this section on Applications, although strictly speaking, at present, they do not yet greatly involve liquid crystal polymers. As the name suggests, a PDLC system consists of low molar mass liquid crystal microdroplets, nematic in most cases, distributed in a solid isotropic polymer matrix. PDLC films are typically formed through the phase separation of an initially homogeneous solution of prepolymer and low molar mass liquid crystal. During the course of the polymerisation, the liquid crystalline material becomes insoluble in the polymer and phase separates, nucleating the formation of approximately micron-sized droplets which are nearly spherical in shape.

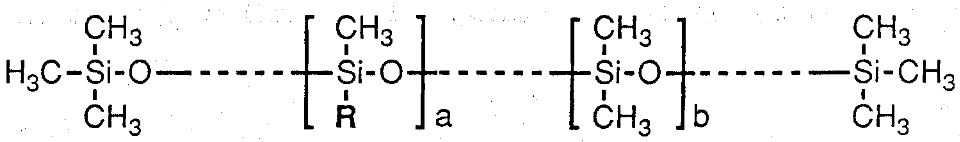
It is largely due to the unique electro-optical properties exhibited by PDLC systems that such LC/polymer matrices have become attractive for technological applications. In the absence of an external applied field (off-state), there is no preferred macroscopic alignment of the directors within each microdroplet, and in-coming light is scattered. This gives a film of the polymer matrix a white appearance. However when a field of sufficient intensity is applied (on-state), the director of each droplet aligns along a preferred direction parallel to the field, if $\Delta\varepsilon$ for the LC material is positive, and if the refractive index ($n_{||}$) of the liquid crystal is matched to that of the isotropic polymer, the film appears transparent. On removal of the field, the large surface area-to-volume ratio of the microdroplets allows surface interactions to return the LMM material to its random alignment and the opaque texture is again displayed. In this way, the film can be switched from a light scattering to a clear state by the application of an external field of appropriate strength.

These materials offer new concepts in the fabrication of display devices. The PDLC film, which is flexible, can be processed to any size, thickness and form. Furthermore, polarisers are not required and this brings simplicity to display cell manufacture, while allowing for improved brightness and contrast. In addition to display applications, PDLC systems are considered interesting materials for surface induced second harmonic generation [111]. There have also been recent developments concerning the use of droplets of LMM liquid crystals in a LCP matrix, and these films are claimed to give better alignment and clarity of the on-state [112].

## 1.5 AIMS

Side chain liquid crystal polysiloxanes are prepared by a poly(hydrosilylation) reaction between a preformed polysiloxane backbone with reactive Si-H sites and a mesogenic alkene, in the presence of a platinum catalyst. Originally, the rod-like mesogenic group was appended to the backbone, *via* the flexible spacer, by its terminus, forming a comb-like structure. Quite recently, the idea was conceived of appending the mesogenic group to the backbone, again *via* a flexible spacer, in such a way that the axis of the rod-like group lies in the direction of the backbone. Such LCP have become known as laterally attached side chain LCP. The literature appears to suggest that these polymers have a very strong disposition to be nematic. This is a considerable advantage, as the terminally attached analogues have a rather overweaning tendency to be smectic, particularly when interesting terminal groups such as cyano are present in the mesogenic group.

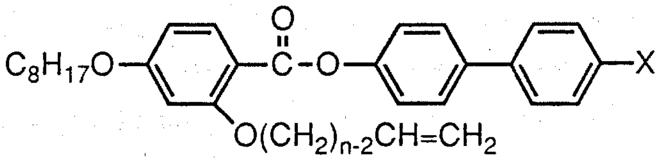
The initial aim of the research was to develop a reliable and reproducible method for the preparation of laterally attached side chain liquid crystal polysiloxanes -- both of the side chain homopolymer and copolymer type, as well as of the backbone homopolymer and copolymer variety. These had the general stucture:



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O\text{------}\left[\overset{CH_3}{\underset{R}{Si}}-O\right]_a\text{------}\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_b\text{------}\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

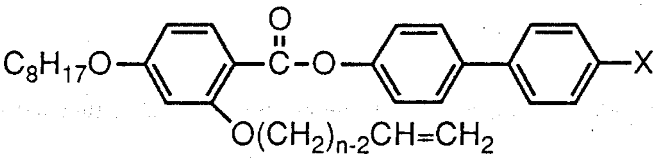
b = 0, backbone homopolymer **(W)**
b > 0, backbone copolymer **(P)**

**R** - from one kind of mesogenic alkene precursor; side chain homopolymer
**R** - from a mixture of mesogenic alkene precursors; side chain copolymer



This required the systematic investigation of all the factors involved in the synthesis of these materials -- catalyst type and amounts needed, solvent effects, reaction conditions and time, monitoring of reaction progress and purification of the final polymer. These polymers had to be fully characterised, by techniques such as thermal analysis, optical microscopy, gel permeation chromatography, as well as by dielectric permittivity and x-ray diffraction studies. An extensive study was also to be undertaken, to observe the effect of molecular weight and polydispersity of the SCLCP on phase transition temperatures of both terminally and, for the first time on any backbone, laterally attached SCLCP.

Using a novel mesogenic group, with an unusually asymmetric point of linkage along the molecular long axis to bond the side chain to the polymer main chain *via* the flexible spacer, laterally attached SCLCP were to be synthesised.



The research was geared towards the production of SCLCP that exhibit room temperature nematic phases with positive dielectric anisotropies, since this allowed for the possible use of laterally attached SCLCP in speciality applications. Much attention was thus focussed on the use of terminally cyano-substituted mesogenic groups on the highly flexible polysiloxane backbone, for it was envisaged that the favourably high dielectric properties of the side chain would be conferred upon the polymer, thereby minimising threshold voltages in devices. However, the presence of terminal cyano-groups introduces the problem of antiparallel correlations, a result of the formation of interdigited bilayer structures caused by the overlap of the highly polar end-groups. This has the effect of reducing the overall dipole moment and hence the dielectric properties of the system. Attempts, therefore, had to be made to reduce this effect, so as to maximise the dielectric properties of the resultant polymer.

Further to the work developed within this Group on side chain copolymers with conventionally and laterally attached side chains, this area was to be extended to cover a larger variety and combination of side chains, to give interesting characteristics that may be otherwise difficult to achieve in either homopolymer system. It was hoped that this type of mixed copolymer system would be found to offer greater control and flexibility over the fine tuning of liquid crystalline properties.

By altering the nature of the end-group on the side chain, or by the modification of the mesogenic core, a range of side chain polymers would be synthesised. This would allow the establishment of structure-property relationships, with particular regard to $T_{N-I}$ values -- this being the only phase type identified to date in studies on laterally attached SCLCP. The data collected could then be used in correlations with the known effects for low molar mass materials, so allowing possible future tailoring of the properties of SCLCP.

From an academic viewpoint, the objective of this project was to augment and expand upon the small number of laterally attached SCLCP currently recorded in the literature, through the production of novel materials for physical study. Unlike those of their terminally attached analogues, the characteristics of this new class of SCLCP are still not well defined, and the number of subsequent publications since they were first synthesised has remained small, particularly if polysiloxanes alone are considered.

## 1.6 REFERENCES

1. F. Reinitzer, *Monatsh. Chem.*, **9**, 421 (1888).
2. O. Lehmann, *Z. Phys. Chem. (Leipzig)*, **4**, 462 (1889).
3. G. Friedel, *Ann. Phys. (Paris)*, **18**, 273 (1922).
4. F.D. Saeva, *"Liquid Crystals: The Fourth State of Matter"*, Marcel Dekker, New York and Basel (1979).
5. L. Onsager, *New York Acad. Sci.*, **51**, 627 (1949).
6. A. Ishihara, *J. Chem. Phys.*, **18**, 1446 (1950).
7. P.J. Flory, *Proc. R. Soc. London*, Ser. A **234**, 73 (1956).
8. R.J. Young, *"Introduction to Polymers"*, Chapman and Hall, London (1986).
9. S. Friberg, *"Lyotropic Liquid Crystals"*, Advances in Chemistry, Vol. 152, ACS, Washington DC (1976).
10. G.W. Gray and P.A. Winsor, *"Liquid Crystals and Plastic Crystals"*, Vol. 1, Ellis Horwood, Chichester (1974).
11. H. Sackmann and D. Demus, *Mol. Cryst. Liq. Cryst.*, **21**, 239 (1973).
12. A.C. Griffin and S.J. Havens, *J. Polym. Sci., Polym. Lett.*, **18**, 259 (1980).
13. H. Finkelmann, H.J. Kock and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **89**, 23 (1982).
14. A.J. Leadbetter, in *"The Molecular Physics of Liquid Crystals"* (eds. G.R. Luckhurst and G.W. Gray), Academic Press, London (1979).
15. G.W. Gray and J.W. Goodby, *"Smectic Liquid Crystals: Textures and Structures"*, Leonard Hill, Glasgow (1984).
16. J. Nehring and A. Saupe, *J. Chem. Soc., Faraday Trans. II*, **68**, 1 (1972).
17. G.W. Gray and D.G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **37**, 189 (1976).
18. F. Grandjean, *C.R. Seances Acad. Sci. (Paris)*, **166**, 165 (1917).
19. P.P. Crooker, *Liq. Cryst.*, **5**, 751 (1989).
20. J.W. Goodby and T.M. Leslie, *Mol. Cryst. Liq. Cryst.*, **110**, 175 (1984).
21. J. Doucet, P. Keller, A.M. Levelut and P. Porquet, *J. Phys. (Paris)*, **39**, 548 (1978).
22. G. Scherowsky, A. Schliwa, J. Springer, K. Kuhnpast and W. Trapp, *Liq. Cryst.*, **5**, 1281 (1989).
23. S. Uchida, K. Morita, K. Miyoshi, K. Hashimoto and K. Kawasaki, *Mol. Cryst. Liq. Cryst.*, **155**, 93 (1988).

24. J.W. Goodby, *Mol. Cryst. Liq. Cryst.*, **92**, 171 (1983).

25. A. Ciferri, in *"Polymer Liquid Crystals"* (eds. A. Ciferri, W.R. Krigbaum and R.B. Meyer), Academic Press, New York (1982).

26. B. Reck and H. Ringsdorf, *Makromol. Chem., Rapid. Commun.*, **6**, 291 (1985).

27. R. Zentel and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, **5**, 393 (1984).

28. B. Hahn, J.H. Wendorff, M. Portugall and H. Ringsdorf, *Colloid Polym. Sci.*, **259**, 875 (1981).

29. J.M. Rodriguez-Parada and V. Percec, *J. Polym. Sci., Polym. Chem.*, **24**, 1363 (1986).

30. F. Cser, K. Nyitrai, J. Horvath and G. Hardy, *Eur. Polym. J.*, **21**, 259 (1985).

31. O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farnham and T.V. Rajan-Babu, *J. Am. Chem. Soc.*, **105**, 5706 (1983).

32. W. Kreuder, O.W. Webster and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, **7**, 5 (1986).

33. M.S.K. Lee and P.J. Smith, unpublished results.

34. M.van Beylen, S. Bywater, G. Smetz, M. Szwarc and D.J. Worsfold, *Adv. Polym. Sci.*, **86**, 87 (1988).

35. P. Keller, *Mol. Cryst. Liq. Cryst.*, **155**, 37 (1988).

36. H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, **1**, 31 (1980).

37. J. Majnusz, J.M. Catala and R.W. Lenz, *Eur. Polym. J.*, **19**, 1043 (1983).

38. A. Roviello and A. Sirigu, *J. Polym. Sci., Polym. Lett.*, **13**, 455 (1975).

39. A. Shanley, *Chemical Business*, **4**, 44 (1989).

40. H. Finkelmann, H. Ringsdorf and J.H. Wendorff, *Makromol. Chem.*, **179**, 273 (1978).

41. V.P. Shibaev, J.S. Freidzon and N.A. Pláte, *Dokl. Akad. Nauk SSSR*, **227**, 1412 (1976).

42. A. Blumstein and E.C. Hsu, in *"Liquid Crystalline Order In Polymers"* (ed. A. Blumstein), Academic Press, New York (1978).

43. P.G. de Gennes, *C.R. Hebd. Seances Acad. Sci.*, Ser. B **281**, 101 (1975).

44. F. Hessel and H. Finkelmann, *Polym. Bull. (Berlin)*, **14**, 375 (1985).

45. V.P. Shibaev, S.G. Kostromin and N.A. Pláte, *Eur. Polym. J.*, **18**, 651 (1982).

46. H. Finkelmann, in *"Polymer Liquid Crystals"* (eds. A. Ciferri, W.R. Krigbaum and R.B. Meyer), Academic Press, New York (1982).

47. J. Frenzel and G. Rehage, *Makromol. Chem.*, **184**, 1685 (1983).

48. N.A. Pláte and V.P. Shibaev, *J. Polym. Sci., Polym. Symp.*, **67**, 1 (1980).

49. N.A. Pláte, V.P. Shibaev, B.S. Petrukhin and V.A. Kargin, *J. Polym. Sci., Part C*, **23**, 37 (1968).

50. A. Blumstein, Y. Osada, S.B. Clough, E.C. Hsu and R.B. Blumstein, in *"Mesomorphic Order In Polymers"* (ed. A. Blumstein), ACS Symposium Series, No. 74, Washington DC (1978).

51. P.L. Magagnini, *Makromol. Chem.*, Suppl. **4**, 223 (1981).

52. M.A. Apfel, H. Finkelmann, G.M. Janini, R.J. Laub, B.H. Luhmann, A. Price, W.L. Roberts, T.J. Shaw and C.A. Smith, *Anal. Chem.*, **57**, 651 (1985).

53. A. Blumstein, S. Vilasagar, S. Ponrathnam, S.B. Clough and R.B. Blumstein, *J. Polym. Sci., Polym. Phys.*, **20**, 877 (1982).

54. H. Stevens, G. Rehage and H. Finkelmann, *Macromolecules*, **17**, 851 (1984).

55. W.D. Hawthorne, Ph.D. Thesis, University of York (1986).

56. P.A. Gemmell, Ph.D. Thesis, University of Hull (1985).

57. H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, **1**, 733 (1980).

58. V.P. Shibaev, V.M. Moiseenko, Ya S. Freidzon and N.A. Pláte, *Eur. Polym. J.*, **16**, 277 (1980).

59. H. Ringsdorf and A. Schneller, *Makromol. Chem., Rapid Commun.*, **3**, 557 (1982).

60. H. Ringsdorf and A. Schneller, *Br. Polym. J.*, **13**, 43 (1981).

61. G.W. Gray, *"Molecular Structure and the Properties of Liquid Crystals"*, Academic Press, London and New York (1962).

62. M. Engel, B. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, H.W. Schmidt and P. Tschirner, *Pure and Appl. Chem.*, **57**, 1009 (1985).

63. P. Keller, *Mol. Cryst. Liq. Cryst.*, **157**, 193 (1988).

64. G. de Marignan, D. Teyssie, S. Boileau, J. Malthète and C. Noel, *Polymer*, **29**, 1318 (1988).

65. K.H. Wassmer, E. Ohmes, M. Portugall, H. Ringsdorf and G. Kothe, *J. Am. Chem. Soc.*, **107**, 1511 (1985).

66. H.W. Spiess, *Pure and Appl. Chem.*, **57**, 1617 (1985).

67. H. Finkelmann, U. Kiechle and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **94**, 343 (1983).

68. K.J. Toyne, in *"Thermotropic Liquid Crystals"* (ed. G.W. Gray), CRAC Series, Vol. 22, John Wiley and Sons, Chichester (1987).

69. W. Kreuder and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, **4**, 807 (1983).

70. G. Wenz, *Makromol. Chem., Rapid Commun.*, **6**, 577 (1985).

71. G.W. Gray and K.J. Harrison, *Mol. Cryst. Liq. Cryst.*, **13**, 37 (1971).

72. D. Coates, G.W. Gray and K.J. Harrison, *Mol. Cryst. Liq. Cryst.*, **22**, 99 (1973).

73. D.J. Byron, G.W. Gray, A. Ibbotson and B.M. Worrall, *J. Chem. Soc.*, 2246 (1963).

74. W. Weissflog and D. Demus, *Crystal Res. Technol.*, **19**, 55 (1984).

75. H. Richard, M. Mauzac, H.T. Nguyen, G. Sigaud, M.F. Achard, F. Hardouin and H. Gasparoux, *Mol. Cryst. Liq. Cryst.*, **155**, 141 (1988).

76. M. Mauzac, F. Hardouin, H. Richard, M.F. Achard, G. Sigaud and H. Gasparoux, *Eur. Polym. J.*, **22**, 131 (1986).

77. Q.F. Zhou, H.M. Li and X.D. Feng, *Mol. Cryst. Liq. Cryst.*, **155**, 73 (1988).

78. P. Keller, F. Hardouin, M. Mauzac and M.F. Achard, *Mol. Cryst. Liq. Cryst.*, **155**, 171 (1988).

79. M.J.S. Dewar and R.S. Goldberg, *J. Org. Chem.*, **35**, 2711 (1970).

80. Q.F. Zhou and H.B. Zhou, *Gaodeng Xuexiao Huaxue Xuebao*, **10**, 1163 (1989).

81. G.W. Gray, J.S. Hill and D. Lacey, *Mol. Cryst. Liq. Cryst. Lett.*, **7**, 47 (1990).

82. M.S.K. Lee, G.W. Gray, D. Lacey and K.J. Toyne, *Makromol. Chem., Rapid Commun.*, **11**, 109 (1990).

83. F. Hessel and H. Finkelmann, *Polym. Bull. (Berlin)*, **15**, 349 (1986).

84. C.B. McArdle, *"Side Chain Liquid Crystal Polymers"*, Blackie, Glasgow (1989).

85. N.A. Pláte, *"Liquid Crystal Polymers"*, (in Russian), Khimia, Moscow (1988).

86. I. Cabrera, H. Ringsdorf, M. Ebert and J.H. Wendorff, *Liq. Cryst.*, **8**, 163 (1990).

87. G.W. Gray, J.S. Hill and D. Lacey, *Angew. Chem. Adv. Mater.*, **101**, 1146 (1989).

88. G.W. Gray, J.S. Hill, D. Lacey and M.S.K. Lee, *Proc. 13th Int. Liq. Cryst. Conf., Vancouver*, Abstract POL-53 (1990).

89. H. Finkelmann, H.J. Kock and G. Rehage, *Makromol. Chem., Rapid Commun.*, **2**, 317 (1981).

90. F.H. Kreuzer, M. Gawhary, R. Winkler and H. Finkelmann, E.P. 0060335 (1981).

91. R.D.C. Richards, W.D. Hawthorne, J.S. Hill, M.S. White, D. Lacey, J.A. Semlyen, G.W. Gray and T.C. Kendrick, *J. Chem. Soc., Chem. Commun.*, 95 (1990).

92. F.H. Kreuzer, A. Andrejewski, W. Haas, N. Haberle, G. Riepl and P. Spes, *Mol. Cryst. Liq. Cryst.*, **199**, 345 (1991).

93. M. Ebert, O. Herrmann-Schonherr, J.H. Wendorff, H. Ringsdorf and P. Tschirner, *Liq. Cryst.*, **7**, 63 (1990).

94. M. Schadt and W. Helfrich, *Appl. Phys. Lett.*, **18**, 127 (1971).

95. J. Constant and E.P. Raynes, *Mol. Cryst. Liq. Cryst.*, **62**, 115 (1980).

96. A. J. Leadbetter, R.M. Richardson and C.N. Colling, *J. Phys. (Paris)*, **36**, 37 (1975).

97. T. Srithanratana, Ph.D. Thesis, University of Hull (1982).

98. V.P. Shibaev, V.G. Kulichikhin, S.G. Kostromin, N.V. Vasileva, I.P. Bravermann and N.A. Pláte, *Dokl. Akad. Nauk SSSR*, **263**, 152 (1982).

99. G.W. Gray, K.J. Harrison and J.A. Nash, *Electron. Lett.*, **9**, 130 (1973).

100. H.J. Coles, *Faraday Discuss. Chem. Soc.*, **79**, 201 (1985).

101. C.B. McArdle, M.G. Clark, C.M. Haws, M.C.K. Wiltshire, A. Parker, G. Nestor, G.W. Gray, D. Lacey and K.J. Toyne, *Liq. Cryst.*, **2**, 573 (1987).

102. B.A. Jones, J.S. Bradshaw, M. Nishioka and M.L. Lee, *J. Org. Chem.*, **49**, 4947 (1984).

103. S.K. Aggarwal, J.S. Bradshaw, M. Eguchi, S. Parry, B.E. Rossiter, K.E. Markides and M.L. Lee, *Tetrahedron*, **43**, 451 (1987).

104. N.A. Pláte and V.P. Shibaev, *Makromol. Chem.*, Suppl. **6**, 3 (1984).

105. H. Finkelmann, *Angew. Chem. Int. Ed. Engl.*, **27**, 987 (1988).

106. H. Hirschmann, D. Velasco and H. Finkelmann, *Proc. 13th Int. Liq. Cryst. Conf., Vancouver*, Abstract NLO-16-P (1990).

107. C. Jones, *Chem. and Ind.*, **19**, 600 (1990).

108. J.R. Hill, P. Pantelis, F. Abbasi and P. Hodge, *J. Appl. Phys.*, **64**, 2749 (1988).

109. G.R. Meredith, J.G. VanDusen and D.J. Williams, *Macromolecules*, **15**, 1385 (1982).

110. J.W. Doane, N.A. Vaz, B.G. Wu and S. Zumer, *Appl. Phys. Lett.*, **46**, 269 (1986).

111. L. Li, H.J. Yuan and P. Palffy-Muhoray, *Mol. Cryst. Liq. Cryst.*, **198**, 239 (1991).

112. J.W. Doane, personal communication.

# two

# *discussion of syntheses*

## 2.1 MESOGENIC SIDE CHAINS

### 2.1.1 Techniques and Characterisation

Transition temperatures were determined by differential scanning calorimetry (DSC), using a Perkin Elmer DSC-2C and Perkin Elmer Thermal Analysis Data Station, and confirmed by optical microscopy, which was also used to identify the mesophase type, using an Olympus BH-2 polarising microscope in conjunction with a Mettler FP52 hot stage and Mettler FP5 temperature control unit. Thermo-optical analysis (TOA) was also carried out, using a Vickers M72C polarising microscope fitted with a photodiode eyepiece connected through a power source to a chart recorder, in conjunction with a Mettler FP82 hot stage and Mettler FP80 Central Processor.

The structures of all intermediates and final products prepared were confirmed by a combination of infra-red spectroscopy (Perkin Elmer 783), $^1$H nuclear magnetic resonance spectroscopy (Jeol JNM-GX270 FT NMR), and gas chromatography/mass spectrometry (Finnigan 1020 Automated GC/MS). Optical rotation measurements were obtained using a polarimeter (Bendix ETL-NPL Automatic Polarimeter Control Unit Type 143A).

Purification of compounds by column chromatography was performed either by normal gravity column chromatography (Fisons 60 - 120 mesh) or flash chromatography (Sorbsil C60 silica gel 40 - 60 microns), eluting in each case with an appropriate solvent system. Important tests for product purity were thin layer chromatography (TLC -- single spot) and sharpness of melting point. TLC was carried out using pre-coated aluminium plates (Merck -- silica gel 60 $F_{254}$, layer thickness 0.2 mm) and an appropriate eluent; plates were then examined under ultraviolet light ($\lambda = 254/365$ nm).
Melting points of materials were obtained using a Gallenkamp melting point apparatus.

In addition, the purities of the side chain precursors were checked by high performance liquid chromatography (HPLC). The following equipment was used: Kontron HPLC Pump 420, Perkin Elmer ISS-100 Auto Sampler, Chrompack Multiport Stream Switch fitted with a Rheodyne valve (injector), Spectroflow 757 Absorbance Detector (variable wavelength) and a Perkin Elmer database. A C18 reverse-phase Microsorb column was used. The mobile phases used were methanol (100%) and methanol:water (volume ratio 95:5). Purities of > 99.5% were generally obtained.

Various abbreviations used in presenting data for phase transitions are:

K = crystalline solid.

S = smectic liquid crystal, where subscripts A and C indicate the respective smectic phase type.

N = nematic liquid crystal.

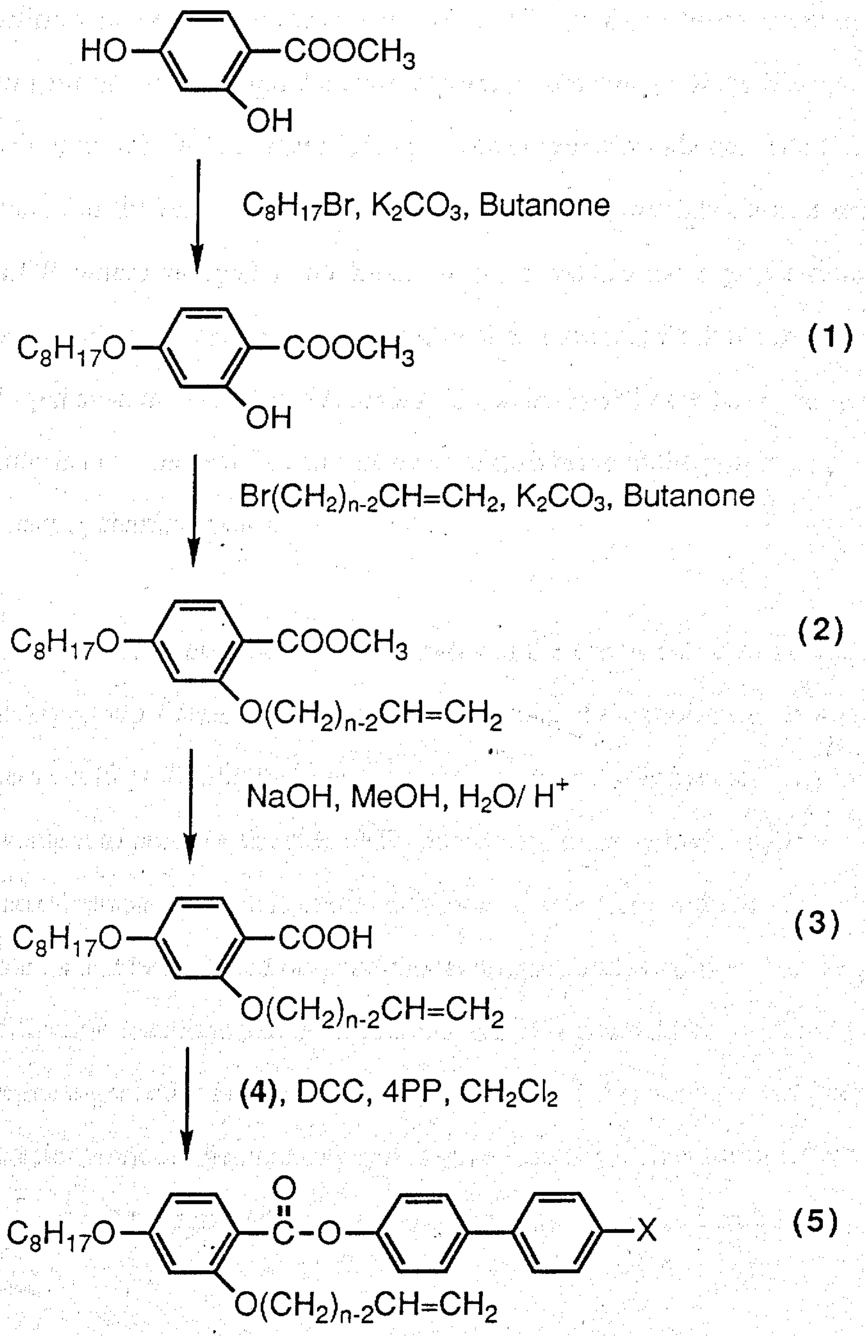
Ch = cholesteric liquid crystal.

I = isotropic liquid.

( ) = round brackets around a transition temperature indicate a monotropic transition.

## SCHEME A

### Synthesis of 4-substituted biphenyl-4'-yl 2-(ω-alkenyloxy)-4-octyloxybenzoates



### 2.1.2 Scheme A - Synthesis of 4-substituted biphenyl-4'-yl 2-(ω-alkenyloxy)-4-octyloxybenzoates

The side chain precursors used in the preparation of laterally attached side chain liquid crystal polysiloxanes and mixed lateral/terminal copolymer systems were synthesised *via* reaction scheme A. The mesogenic side chains produced were novel in terms of both their general structure and the chosen point of attachment of the flexible spacer unit required to link the mesogenic group to the polymer backbone. The lateral position chosen was different from that reported by various other laboratories for this class of SCLCP, where the spacer attachment was located at a more 'gravitationally favourable' point closer to the centre of the molecule, i.e., radiating from the middle ring of a 3-ringed system [1,2]. The precursors, **(5)**, synthesised here have the spacer unit positioned in a more off-centre manner, and so bring to the polymers certain unique and interesting characteristics.

The first series of polymers studied involved the use of side chain precursors with a methoxy group situated at the left hand terminus of the molecule. It was decided that this system could profitably be investigated first, since it was synthetically cheaper and more convenient to produce the side chain precursors from methyl 2-hydroxy-4-methoxybenzoate, which is commercially available from Aldrich. Once any teething problems had been sorted out, and the techniques and conditions for the polymer modification reactions had been established, efforts would be switched to the work on the more mesogenically favourable octyloxy family of compounds. Additionally, however, the earlier work on the methoxy series gave results which contributed towards a broadening of the relatively small knowledge base associated with laterally attached SCLCP.

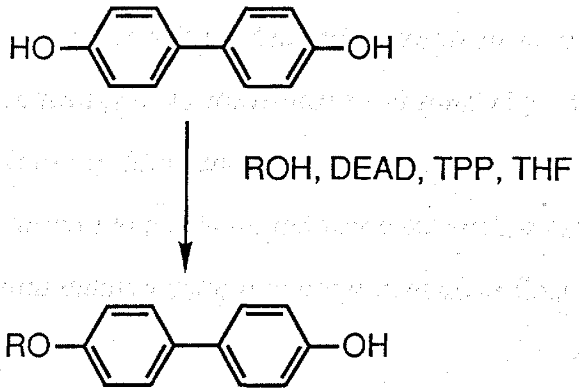
The first step in synthetic route A involved the selective monoalkylation of methyl 2, 4-dihydroxybenzoate with 1-bromo-octane, to give the octyloxy group in the *para*-position of the ring. It was inevitable that a percentage of *ortho*-product would be produced, as well as some dialkylated product. However, the main constituent of the mixture was the required 4-octyloxy compound, no doubt favoured due to steric factors, and this was isolated pure by repeated crystallisations (four on average). The three products were quite easily distinguishable by TLC which was used to monitor the effectiveness of each crystallisation. Yields were generally around 40%, this being attained when the alkyl halide was added dropwise and at an extremely slow rate.

The pure methyl 2-hydroxy-4-octyloxybenzoate was then alkenylated by a similar method, using potassium carbonate in butanone [3]. The phenolic -OH at the 2-position formed the potassium salt, in the presence of a large excess of the carbonate, and allowed nucleophilic substitution of the halogen of the bromo-alkene to occur easily. The ester was next subjected to base catalysed hydrolysis and the side chain precursors were synthesised by DCC esterification of the free acid and the appropriate 4-substituted 4'-hydroxybiphenyl (**4**). This esterification procedure uses dicyclohexylcarbodiimide (DCC) and an aminopyridine catalyst, 4-(*N*-pyrrolidino)pyridine (4PP) [4]. This method was used in preference to more conventional methods of esterification [5], such as that using the acid chloride, because of its efficiency and simplicity. Most esterifications require either the presence of strong acids, the isolation of intermediate acyl derivatives or the application of heat. The DCC reaction proceeds under mild, essentially neutral conditions; it is effectively a 'one-pot' reaction, which takes place at room temperature, and purification of the product is easy. There have been reports, however, of limitations of the method, e.g., variable yields and a tendency in some cases to yield the *N*-acylureas as the final products. These observations, however, have been associated with the use of the carbodiimide on its own. The presence of a basic catalyst is found to give much improved yields at room temperature. 4-*N, N*-Dimethylaminopyridine (DMAP) added at between 3 and 10 mol-% is found to accelerate the reaction to the extent that the formation of side products is suppressed, and good yields of even sterically demanding esters are obtained [6]. The catalyst used in the present work was 4-(*N*-pyrrolidino)pyridine, and this worked equally well. The DCC is converted in the process to dicyclohexylurea (DCU), which is insoluble and was simply filtered off. Column chromatography was then used to isolate the product in high yields, normally in excess of 60%.

Variation of the substituents in the biphenyl ester unit permitted the synthesis of over thirty novel mesogenic side chains, and allowed a systematic examination to be made of the effect of changing the end-groups and core of the mesogenic moiety, i.e., enabling thorough studies to be made of structure-property correlations in the polymers. Much is already known about structure-property correlations in low molar mass systems [7], but effects relating to side chains attached to a polymer backbone, especially when these are attached as laterals, are still relatively uncharted. Some of the 4-substituted 4'-hydroxybiphenyls used in the synthesis of the side chain precursors were obtained either from industrial or personal sources, but many had to be made, by methods which are given in Schemes Ai - v.

## SCHEME Ai

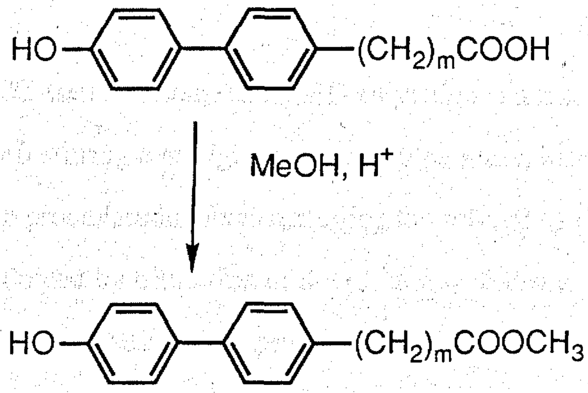
### Synthesis of 4-alkoxy-4'-hydroxybiphenyls



**(4e - q)**

## SCHEME Aii

### Synthesis of methyl 4-hydroxybiphenyl-4'-carboxylate and methyl ω-(4-hydroxybiphenyl-4'-yl) alkanoates



where m = 0, 1 and 2

**(4r, s, t)**

### 2.1.3 Scheme Ai -

### Synthesis of 4-alkoxy-4'-hydroxybiphenyls

This series of compounds was synthesised through the monoalkylation of 4, 4'-biphenol, using the appropriate alcohol, diethyl azodicarboxylate (DEAD) and triphenylphosphine (TPP) [8]. This reaction was used in preference to the normal potassium hydroxide method [9], due mainly to its convenience and simplicity. Yields were comparable, if not improved. The only disadvantage of using this method is the cost involved, DEAD being relatively expensive to purchase, and hence the method cannot be considered for large scale operations unless a marked improvement in the final product yield can be attained to justify its use.

Different sequential orders of adding together the components of the DEAD reaction were tried. Although it was found that this did not in general affect the course of the reaction, the most convenient method was found to be that in which a solution of DEAD in THF is added dropwise to a solution of the alcohol, the biphenol and TPP in THF.
The introduction of the DEAD initiates the alkylation by reaction with triphenylphosphine and formation of an alkoxyphosphonium salt. This is subsequently attacked by the acidic component. Reaction proceeds by $SN_2$ type displacement of triphenylphosphine by the phenolic anion.

Like the DCC esterification, the DEAD alkylation is a 'one-pot' reaction in which the mixture is left stirring overnight, at room temperature, in an anhydrous aprotic solvent. The work-up procedure involves removing the solvent by distillation under reduced pressure, followed by trituration of the residue with ether. This procedure is based upon the knowledge that the required product is soluble in this solvent, whereas both diethyl hydrazinedicarboxylate and triphenylphosphine oxide, the respective reduced and oxidised products of the reagents involved in the reaction, are insoluble and can simply be filtered off. The trituration procedure was then repeated with dichloromethane to remove residual traces of by-products. The soluble products of the reaction were the monoalkylated and the dialkylated biphenol. In addition, traces of the biphenol starting material were present. Isolation of the required monoalkylated product was not too difficult in this case, although problems have been encountered with other systems synthesised using this technique. Column chromatography (silica gel), eluting with dichloromethane, was able to separate the dialkylated form, which was eluted from the column first, followed by the required monoalkylated product.

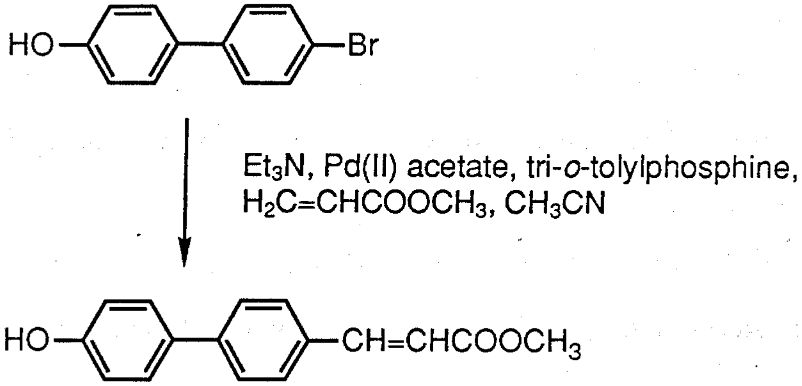
### 2.1.4 Scheme Aii - Synthesis of methyl 4-hydroxybiphenyl-4'-carboxylate and methyl ω-(4-hydroxybiphenyl-4'-yl) alkanoates

4-Hydroxybiphenyl-4'-carboxylic acid and 2-(4-hydroxybiphenyl-4'-yl)ethanoic acid were supplied by BDH Limited, and 3-(4-hydroxybiphenyl-4'-yl)propanoic acid was synthesised by Dr A.W. Hall.

These acids were esterified by boiling overnight in methanol, which served both as solvent and esterifying agent, together with a few drops of concentrated sulphuric acid to catalyse the reaction. Some molecular sieves were also introduced to mop up water formed and shift the equilibrium towards products. The reaction was monitored to a point as close to completion as possible (TLC), but there were inevitably traces of unreacted acid left. To avoid complications at the next stage of the synthesis, i.e., in the DCC esterification between these substituted hydroxy esters and compound **(3)** in Scheme A, it was crucial that the product be isolated free from starting material. This was achieved by washing with saturated sodium bicarbonate solution, followed by extraction of the pure hydroxy ester into dichloromethane.

## SCHEME Aiii

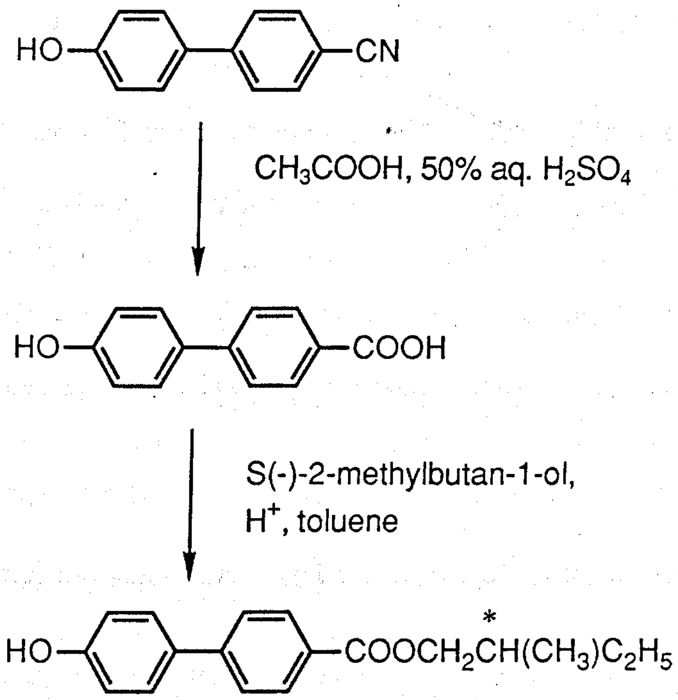
### Synthesis of methyl 3-(4-hydroxybiphenyl-4'-yl)acrylate



(4u)

## SCHEME Aiv

### Synthesis of 2-methylbutyl 4-hydroxybiphenyl-4'-carboxylate



(A1)

(4w)

### 2.1.4 Scheme Aiii -

### Synthesis of methyl 3-(4-hydroxybiphenyl-4'-yl)acrylate

This side chain precursor was synthesised by a Heck reaction [10], which involved the addition of an alkene to an aryl system. This was achieved by treatment of an aryl bromide with a palladium-triarylphosphine complex. These palladium-catalysed arylations are believed to proceed by way of π-allylic palladium halide intermediates [11]. The purpose of this particular preparation was to investigate the effect of extending the conjugation of the system, and hence the polarisability of the molecule, on the phase transition temperatures. Although the reaction generally gives a mixture of products, purification in this case was achieved effectively in the work-up, and crystallisation from acetonitrile afforded the required compound free from impurities (single spot -- TLC).

### 2.1.4 Scheme Aiv -

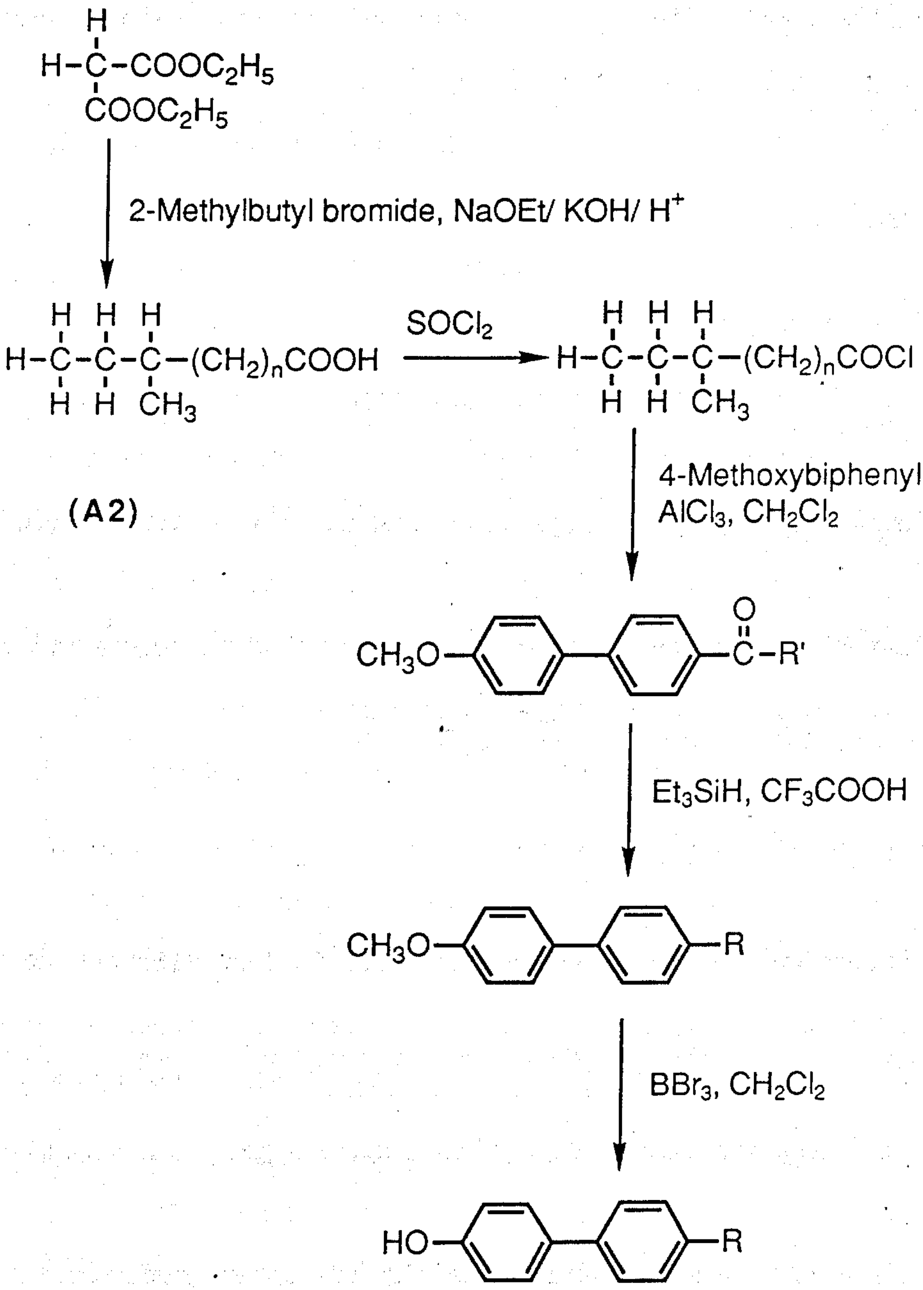
### Synthesis of 2-methylbutyl 4-hydroxybiphenyl-4'-carboxylate

In order to obtain the carboxylic acid that was required for esterification with S(-)-2-methylbutan-1-ol, the first step involved hydrolysis of the nitrile functional of 4-cyano-4'-hydroxybiphenyl to the acid. The reaction was acid-catalysed, to ensure isolation of the hydrolysis product as the acid, and not the amide, which is formed as a reaction intermediate. An addition intermediate is initially obtained, which tautomerises to the amide. The amide is then protonated on the oxygen, and hydrolysis is consequently achieved by a second nucleophilic attack on the positive carbon atom.

The esterification step was conducted in accordance with the procedure described in Scheme Aii, using dry toluene as solvent. Although the acid was only sparingly soluble in this solvent, the reaction was observed to proceed close to completion after prolonged reflux, as monitored by TLC.

## SCHEME Av

### Synthesis of 4-alkyl-4'-hydroxybiphenyls



**(A2)**

**(A3)**

**(A4)**

**(4x, y)**

## 2.1.7 Scheme Av -

## Synthesis of 4-alkyl-4'-hydroxybiphenyls

4-Methylhexanoic acid was synthesised by first adding diethyl malonate to a solution of sodium ethoxide in ethanol. Removal of a proton generated the powerful nucleophilic carbanion which was then able to displace bromide ion from 2-methylbutyl bromide, and give rise to the C-alkylated diethyl ester. The diester was next saponified to the potassium salt of the diacid by boiling in potassium hydroxide solution; addition of concentrated hydrochloric acid and boiling resulted in decarboxylation of the free dicarboxylic acid to give the required acid.

3-Methylpentanoic acid was supplied by BDH Limited.

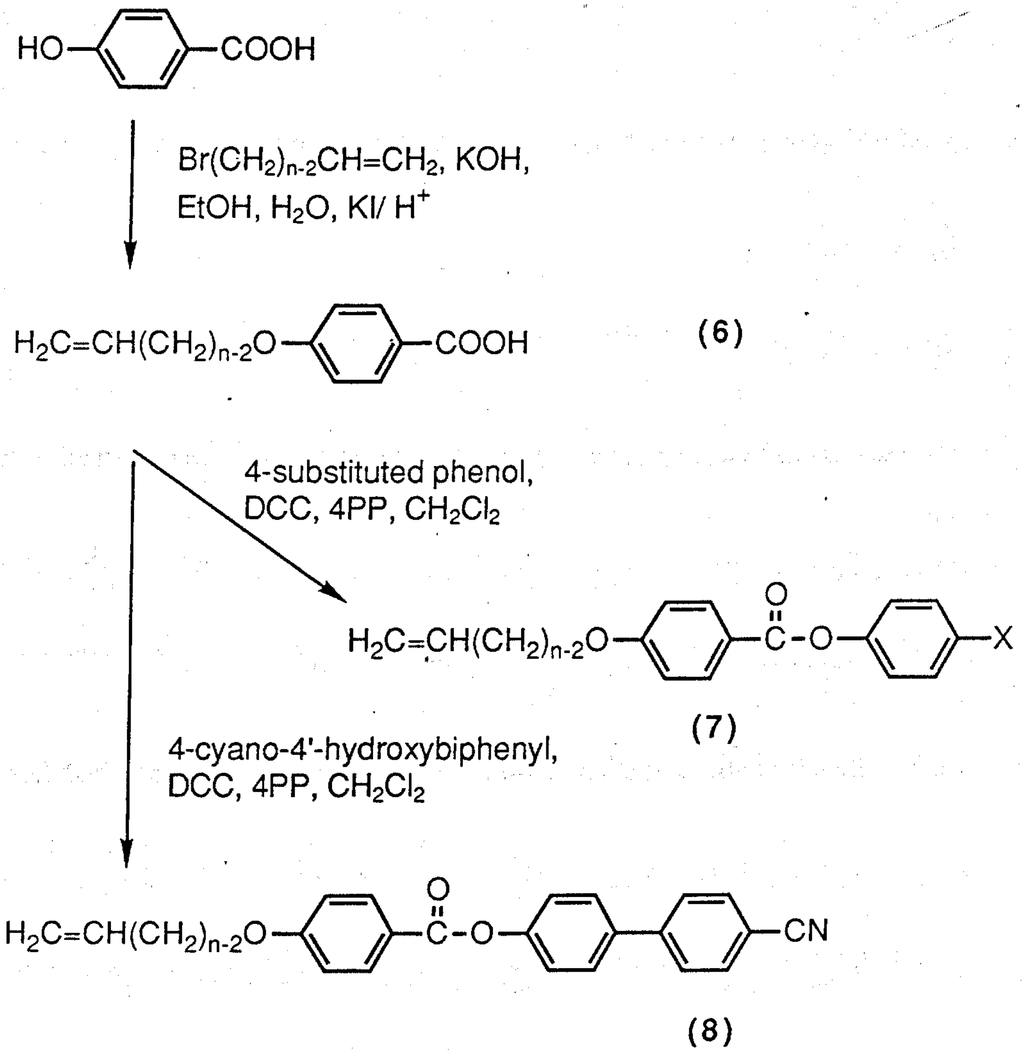
The branched acids were converted into the acid chlorides by boiling with thionyl chloride and then reacting the acid chlorides with 4-methoxybiphenyl to prepare the aryl ketones by the Friedel-Crafts reaction [12], in the presence of ground aluminium chloride, which served as a Lewis acid catalyst. The *ortho/para* directing effect of the methoxy group produced mainly the *para*-product, but a number of by-products were obtained which made separation difficult. These included some *ortho*-isomer [13]. Purification was achieved by column chromatography, and several columns were necessary.

The ketone was reduced using triethylsilane and trifluoroacetic acid [14], a procedure used in preference to the Huang-Minlon modification of the Wolff-Kishner reaction because of its convenience and mild reaction conditions. The silane reduction is remarkably selective, for it is able to reduce the carbonyl group of arylcarbonyl compounds to methylene without affecting other functionalities. The reaction was rapid; in most cases full reaction was obtained in less than 15 minutes, and this was achieved by stirring the reactants at room temperature. The trifluoroacetic acid acts both as a source of protons needed for the reduction and as an efficient solvent. A co-solvent could have been employed, but it has been reported to lower both the rate of reduction and the yield.

Ethers can be cleaved by heating with concentrated hydrobromic acid or with Lewis acids such as $BF_3$ or $AlCl_3$. The method used here to demethylate the alkoxybiphenyl, in order to obtain the phenolic functionality, involved a modification of a technique reported by Niwa *et al.*, using $BBr_3$ as the reagent [15]. Unsatisfactory cleavage reactions involving $BBr_3$ alone have been reported, but these occur with aliphatic and not aromatic methyl ethers, such as those involved here. A reagent system used in the literature to overcome the difficulties with purely aliphatic ethers is one of three equivalents of $BBr_3$ to a NaI-15 crown 5 complex. The iodide anion was probably required to act as a stronger nucleophile for the cleavage of the aliphatic ether systems.

# SCHEME B

## Synthesis of 4-substituted phenyl 4-ω-alkenyloxybenzoates and 4-substituted biphenyl-4'-yl 4-ω-alkenyloxybenzoates



### 2.1.8 Scheme B -

### Synthesis of 4-substituted phenyl 4-ω-alkenyloxybenzoates and 4-substituted biphenyl-4'-yl 4-ω-alkenyloxybenzoates

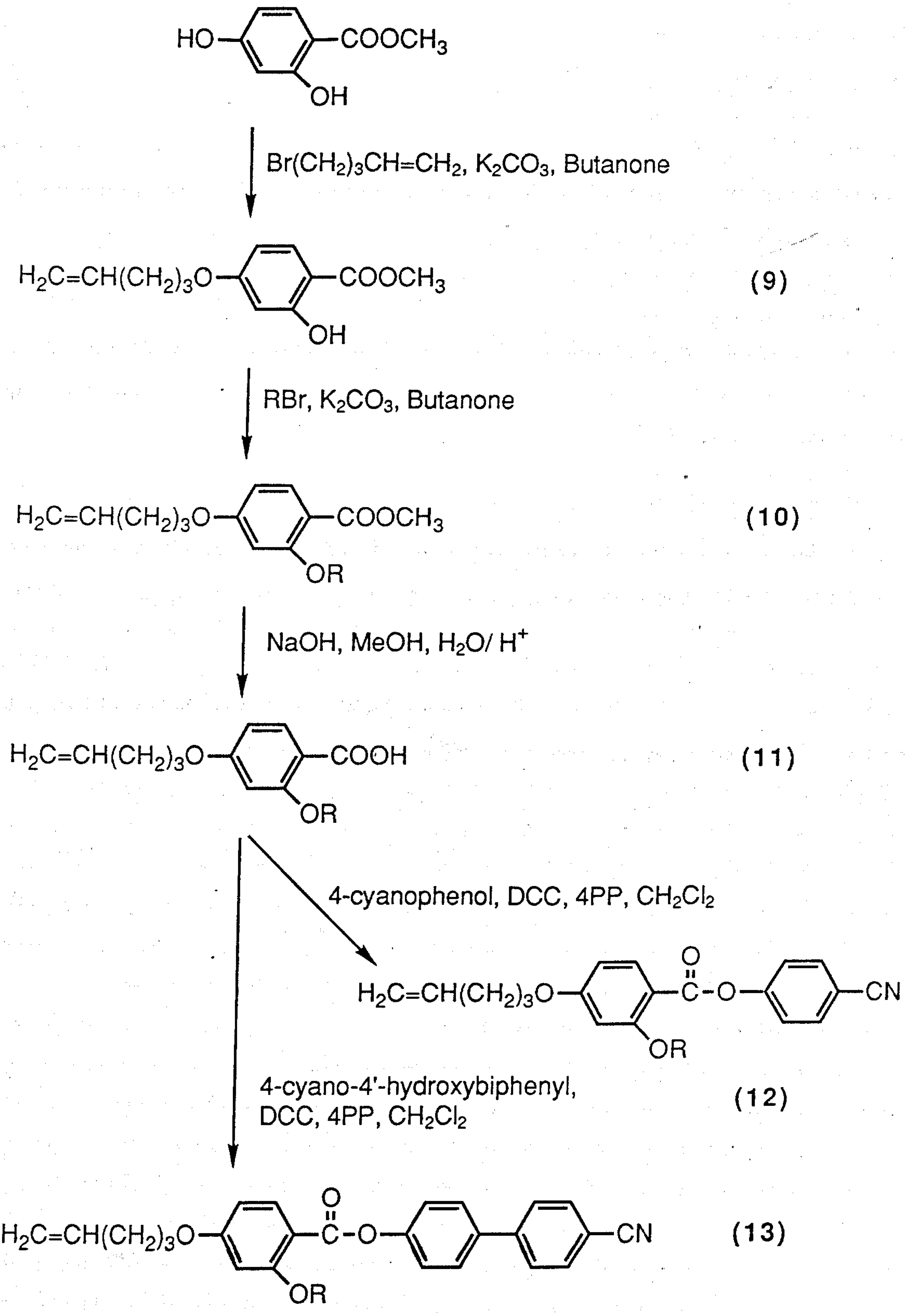
The preparation of these precursors for terminal attachment of side chains has been reported in the literature [16, 17]. They and their polymers were synthesised largely for comparisons with the laterally substituted products from Scheme C and the derived polymers. Furthermore, they were appended as side chains on a number of poly(hydrogenmethylsiloxane) backbone fractions, to examine the effect of molar mass on terminally attached SCLCP. They were also used, together with laterally attached side chains, to form new copolymers incorporating both types of appendage of the mesogenic side groups.

4-Hydroxybenzoic acid was alkenylated by heating with the appropriate alkenyl bromide in alcoholic potassium hydroxide [9]. The potassium carbonate method could not be used here as the mild basic conditions would result in the formation of too much ester. Some ester was formed using the KOH/EtOH method, but subsequent addition of more potassium hydroxide solution and heating, followed by the addition of concentrated hydrochloric acid, hydrolysed this ester and protonated the carboxylate anion giving the free acid. A small amount of potassium iodide was found to catalyse the reaction. The iodide anion, being a stronger nucleophile than the bromide of the alkenylating agent, plays a part in the equilibrium process and encourages alkenylation.

As before, the DCC esterification method was used to generate the final products.

## SCHEME C

### Synthesis of 4-cyanophenyl 2-alkoxy-4-ω-pentenyloxybenzoates and 4-cyanobiphenyl-4'-yl 2-alkoxy-4-ω-pentenyloxybenzoates



### 2.1.9 Scheme C -
### Synthesis of
### 4-cyanophenyl 2-alkoxy-4-ω-pentenyloxybenzoates and
### 4-cyanobiphenyl-4'-yl 2-alkoxy-4-ω-pentenyloxybenzoates

The compounds synthesised in this scheme were required as precursors for terminally attached mesogenic groups which carried lateral alkoxy substituents of increasing length. These lateral alkyl chains were envisaged as lying along the long axes of the mesogenic group. The rationale behind the production of this series was that the lateral groups would, by their steric presence, hinder association of the polar terminal cyano-groups. This would render antiparallel correlations ineffective, thereby increasing the positive dielectric anisotropy [18].

The techniques used in this reaction scheme have already been covered in the preceding sections. It was interesting to find, however, that the first step in this synthesis, the selective monoalkylation of methyl 2, 4-dihydroxybenzoate with 5-bromopent-1-ene, gave consistently higher yields, compared to the analogous preparation using 1-bromo-octane in Scheme A. The terminal alkenic function possibly causes a greater steric effect in relation to attack on the *ortho*-hydroxy group, a factor that could have been responsible for the higher percentage of the *para*-substituted ether formed.

## 2.2 LIQUID CRYSTAL POLYMERS

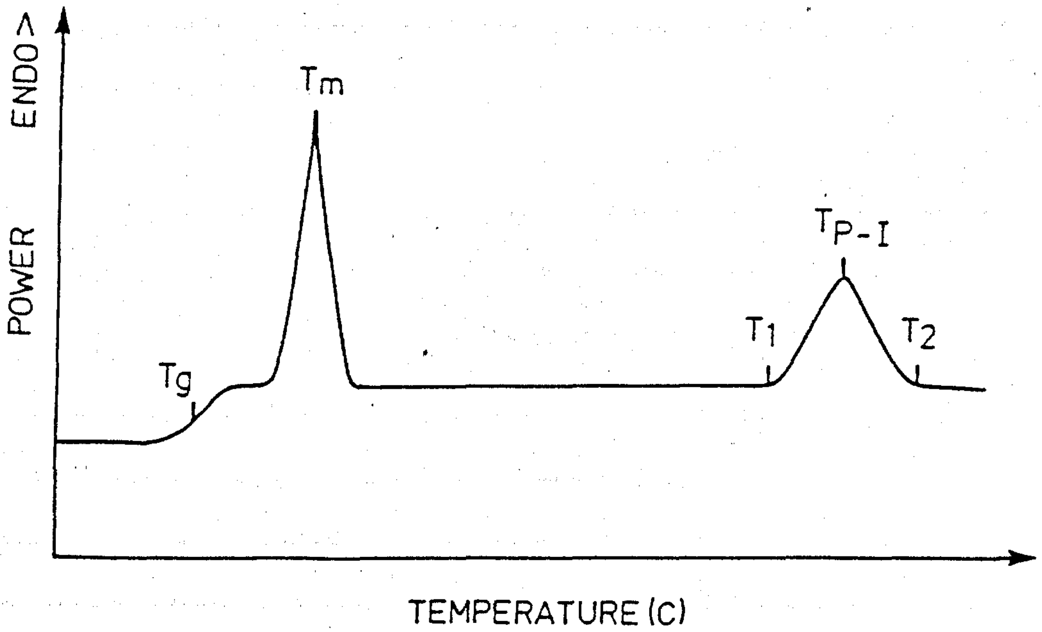
### 2.2.1 Techniques and Characterisation

As with the mesogenic side chains, the SCLC polysiloxanes were examined by optical microscopy. Although textures and phase changes were distinguishable after sample annealing -- the process by which a thin layer of the mesophase was held for periods of several hours at a constant temperature just below its clearing point, in order to obtain a more characteristic textural appearance for the phase -- it was often difficult to determine precise phase transition temperatures. Due to the polydispersity and the viscous nature of the polymers, the phase transitions were usually found to occur over a considerable temperature range, the biphasic region, and this made it difficult to quantify through human judgement. As a result, differential scanning calorimetry (DSC) was often the preferred and most convenient method for obtaining phase transition temperatures.

The DSC pan containing the preparation (*ca.* 6 mg) was first subjected to several rapid heating and cooling cycles (typically from -30 °C to 120 °C @ ± 20 °C $\text{min}^{-1}$). This was done to achieve good thermal contact between the polymer and the pan, thus ensuring that realistic transitions were recorded. The procedure also guaranteed a constant thermal history for all materials. Each subsequent heating and cooling cycle was conducted at 10 °C $\text{min}^{-1}$, with appropriate data being collected on the heat run. The glass transition temperature (Tg) was measured as the midpoint of the characteristic 'jump' in the baseline, and the maximum of the endotherm was taken as the phase transition temperature (Figure 2.1). The extent of the biphasic region, referred to above, was given by the peak width, i.e., the temperature range from onset to completion of a phase transition, *via* the maximum. The results obtained from cooling cycles were also very important, serving to confirm mesophase transitions (which occur with little supercooling), and helping to distinguish these from any transitions involving a crystalline state of the polymer. Such melting transitions do occur on cooling, but usually with extensive supercooling. The recording of cooling cycles, generally, is also of paramount importance, in order to establish whether monotropic mesophases are exhibited.

The polydispersities (γ) of the polymers were checked, after hydrosilylation, by gel permeation chromatography (GPC). This was performed to ensure that there had not been any fractionation or any drastic modification to the spread of molecular weights from that known for the prepolymer to that of the purified mesogenated polymer. The equipment used was similar to that reported for HPLC in Section 2.1.1. The columns used were the G2000 HXL column, in tandem with the G4000 HXL column, both of which contained TSK Gel. The molecular weights were then obtained relative to polystyrene standards.

The centrifuge used for the precipitations to purify polymers after hydrosilylation was a Denley BS400; a spinning speed of 4 500 r.p.m. was usually employed.



Tg = glass transition temperature
Tm = melt temperature
$T_{P\text{-}I}$ = transition temperature from phase to isotropic liquid
$T_1$ = onset of phase transition
$T_2$ = finish of phase transition
PW = baseline peak width ($PW = T_2 - T_1$)

***Figure 2.1***

*Idealised example of a differential scanning calorimetry trace for a crystalline side chain liquid crystal polysiloxane*

### 2.2.2 The Polysiloxane Backbone

Since commercially available polysiloxane backbones are often produced to meet the viscosity requirements of a particular application, rather than a controlled average molecular weight and polydispersity, the polymers normally contain low molar mass cyclic and linear oligomers, together with high molecular weight material, i.e., they are polydisperse. As a result, these polymers often have to be cleaned and purified to limit the sample to a narrower range of molecular weights and achieve a lower polydispersity ($\gamma$). These are important factors to be considered in order to create a consistent information base upon which to formulate credible results for comparative purposes. The number of different batches of polysiloxane backbone used should also be minimised as far as possible, since variations in backbone composition exist even from similar sources. Furthermore each sample lot must be characterised, to allow comparisons to be made of the physical properties of side chain polymers derived from preformed backbones with different origins.

The samples of poly(hydrogenmethylsiloxane) (PHMS) homopolymer backbone used all originated from a single consignment from Wacker Chemie (Munchen, Germany), whilst the poly(hydrogenmethyldimethylsiloxane) [P(HM/DM)S] copolymer backbone was obtained through Petrarch (Karlsruhe, Germany). These materials were used directly, without the need to apply purification methods that remove unwanted lower molecular weight materials [19, 20], since they already had a fairly low polydispersity. This was ascertained by analytical gel permeation chromatography (GPC) and end-group analysis using $^1$H NMR. Important parameters for the prepolymers used are given below.

| | | GPC | | | $^1$H NMR | |
|---|---|---|---|---|---|---|
| | | $\overline{Mw}$ | $\overline{Mn}$ | $\overline{Mw}/\overline{Mn}$ ($\gamma$) | $\overline{Mn}$ | $\overline{DP}$ |
| Wacker Chemie | (W) | 8050 | 3500 | 2.3 | 2920 | 46 ± 3 |
| Petrarch PS122.5 | (P)* | 2400 | 1300 | 1.9 | 1100 | 13 ± 2 |

* Ratio -SiHMeO-:-SiMe$_2$O- = 1:1.17

Stevens *et al.*[21], on the basis of their study of the extent to which the degree of polymerisation influences the phase behaviour of monodisperse side chain LC polysiloxane oligomers, propose that the most drastic differences in transition temperatures are observed for oligomers with $\overline{DP} < 10$. They report only slight thermal variations within the $\overline{DP}$ range 10 - 100, and a seemingly complete independence of $\overline{DP}$ for systems where $\overline{DP} > 100$. As both backbones used in this work had $\overline{DP}$ values in the second range (the $\overline{DP}$ values for the PHMS and P(HM/DM)S prepolymers were 46 and 13 respectively), this would imply that the side chain polymers belong to the range within which the degree of polymerisation would exert a minimal effect on the thermal properties of the liquid crystalline materials. However, significant variations in transition temperatures have been found to occur even up to $\overline{DP} > 100$. In addition, differences in the polymer polydispersity have similar consequences[19]. These two factors reinforce the need for proper backbone prepolymer characterisation, if reproducible side chain systems are to be obtained with properties upon which comparisons can be based.

To enable a study of the effects of low polydispersity and different molecular weights on the liquid crystalline properties of side chain polysiloxanes, fractions of poly(hydrogenmethylsiloxane) with a polydispersity of 1.2 or less and of known molar mass and known number of repeat units ranging from 10 to 250 were obtained. These carefully fractionated or distilled polysiloxane fractions were supplied by courtesy of the York University Polymer Group, where the parameters for the monodisperse fractions were obtained *via* a computer program written to handle data from traces produced by gel permeation chromatography.

### 2.2.3 Preparation Of Liquid Crystalline Polysiloxanes

Side chain liquid crystalline polysiloxanes were prepared by a poly(hydrosilylation) reaction between the prepolymer and the appropriate side chain precursor, a terminal alkene (Scheme D). The alkene was employed in a 10% molar excess to encourage full occupation of the Si-H sites on the polymer backbone [20, 22]. The reaction was therefore a polymer modification process, i.e., no actual polymerisation was involved. By the attachment of a terminal alkene bearing a mesogenic unit to the reactive sites of a preformed polymer backbone, in the presence of a platinum catalyst, the polydispersity and $\overline{DP}$ of the final product were predetermined, since there was no evidence for polymer fractionation or fragmentation during the hydrosilylation process or work-up procedure [23].

The progress of reaction was followed by infra-red spectroscopy on samples obtained from the reaction mixture at appropriate time intervals; the gradual reduction of the Si-H absorption at 2160 $cm^{-1}$ in the spectrum was indicative of the sites being taken up by the side chains. Despite the fact that Apfel *et al.* had switched from infra-red spectroscopy to $^1H$ NMR [$\delta$(p.p.m.) 4.6] in order to monitor their hydrosilylation reactions [20], it has been found in these laboratories that the former method remains the preferred, as well as the most convenient and effective method for analysis [24]. The reaction mixture itself is a dilute solution in toluene and gives only weak absorption levels that make it difficult to ascertain correctly the amount of unreacted Si-H. However by forming an evaporated film of the reaction mixture on the KCl disc used for the analysis, this problem is overcome. When side chains bearing cyano-substituents are used, the C≡N absorption at 2230 $cm^{-1}$ may be used as a convenient reference peak and its absorption level, relative to the Si-H absorption, may be used to express the extent of the reaction as a percentage of its completion (Figure 2.2). This is possible on the basis of observed C≡N/Si-H ratios of absorption obtained with prepared standards [25]. For those mesogenic side chains which do not possess the convenience of this 'built-in indicator', a more qualitative decision may have to be reached from the infra-red spectra as to whether reactions can be safely stopped for subsequent work-up, but with the side chains used in this work, the spectroscopic relationship between the Si-H absorption and that of the C=O of the ester group is also helpful.

Oct-1-ene 'mop-up', a technique used by some research workers to occupy remaining unreacted Si-H sites by octyl groups [17], thereby preventing cross-linking during work-up, was not used. This procedure was not favoured, since introduction of the octyl groups effectively converts the polymer into a side chain copolymer. Although comparative studies between polymers made with and without using this 'mop-up' technique have shown little or no difference in thermal characteristics [25], other physical properties may have been altered, i.e., viscoscity, elastic properties, dielectric anisotropy etc. As the reactions were monitored as far as possible to completion, very few unreacted Si-H sites were to be expected. To substantiate this assertion, there was no evidence that any cross-linking occurred during work-up, as indicated by the continued solubility of the polymers in dichloromethane.

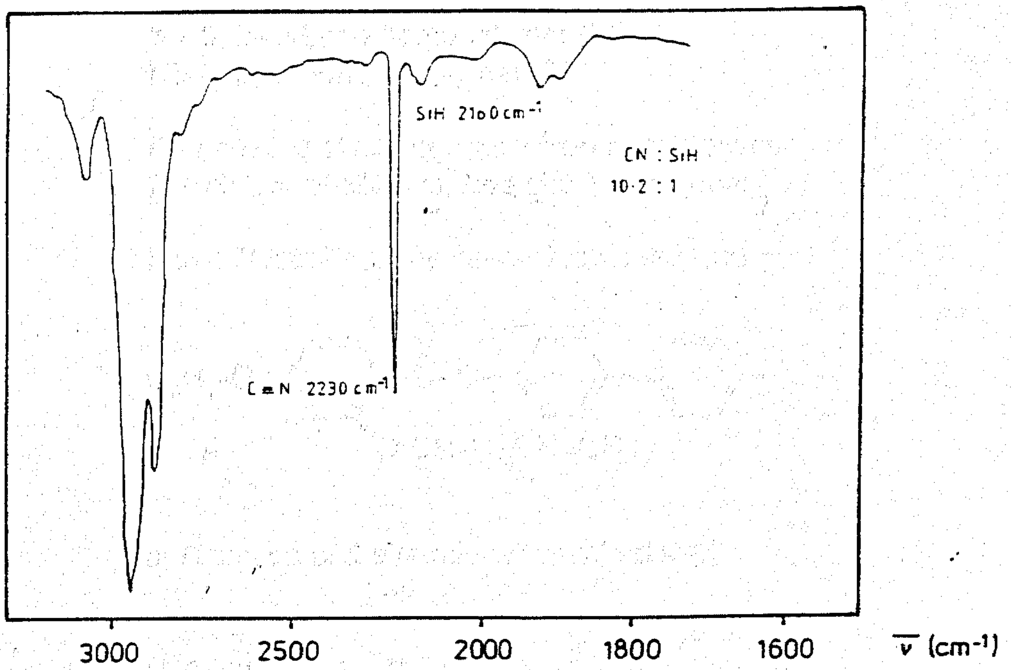
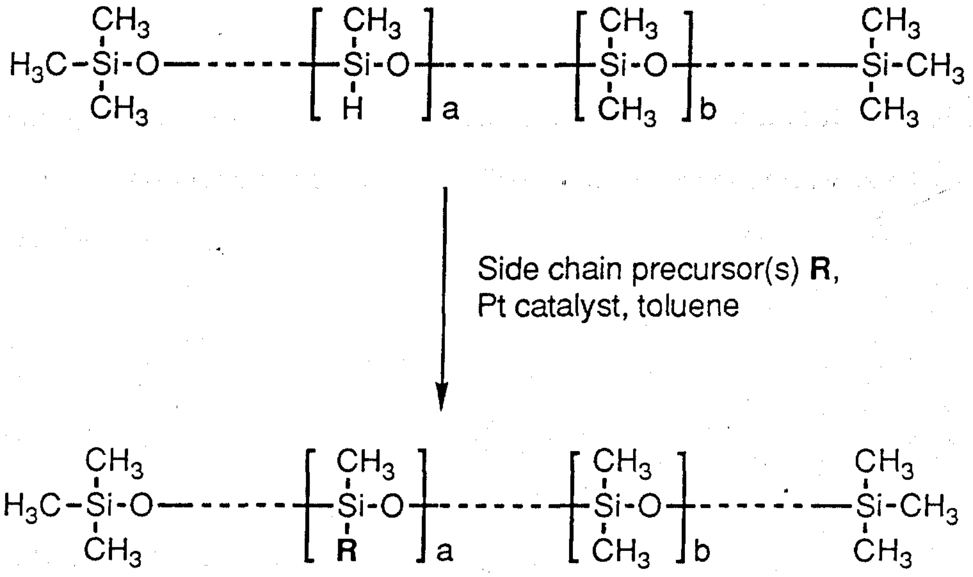


*Figure 2.2*

*Example of the infra-red spectrum of a polymer obtained using an evaporated film of the reaction mixture*

## SCHEME D

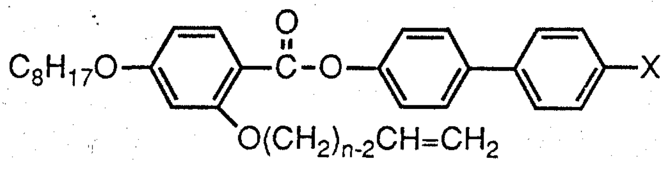
### Synthesis of side chain liquid crystalline polysiloxanes by the poly(hydrosilylation) reaction



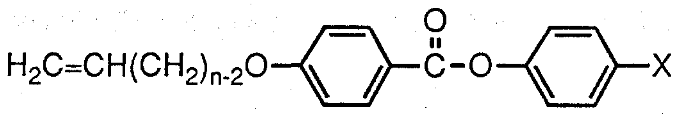
b = 0, backbone homopolymer **(W)**
b > 0, backbone copolymer **(P)**

**R** - one kind of alkene, side chain homopolymer
**R** - mixture of alkenes, side chain copolymer

Either **R** can be of the laterally attached kind



or **R** can be of the terminally attached kind



or a combination of both.

### 2.2.4 Catalyst and Solvent Effects

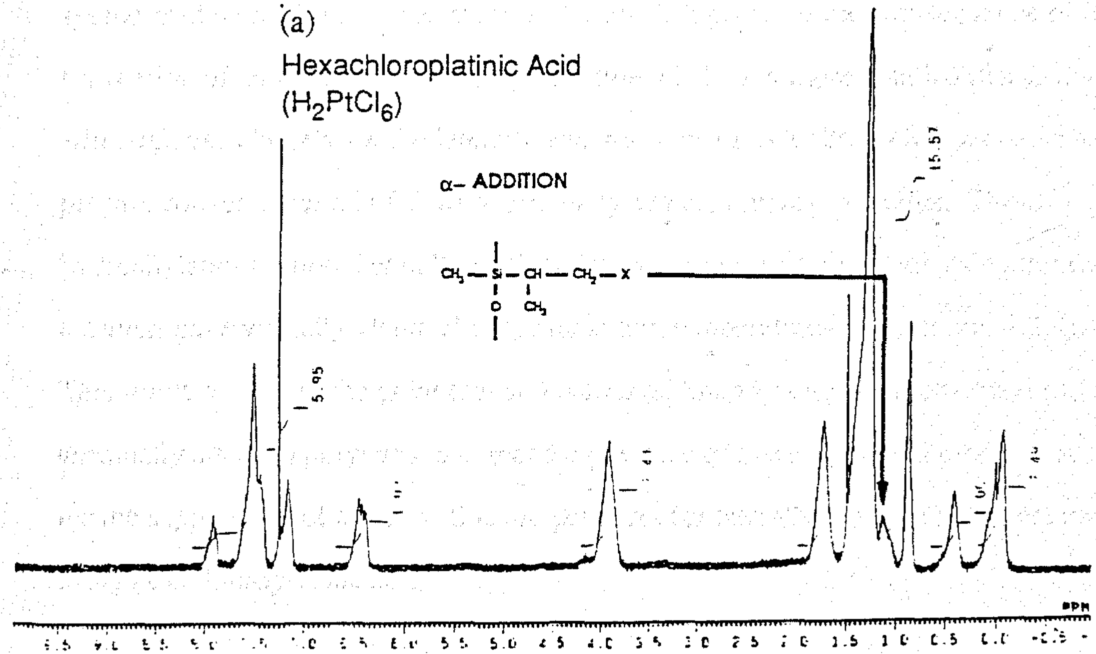
The hydrosilylation reaction was initially performed using techniques established by earlier workers at Hull for preparing LCP with terminally linked side chains and using hexachloroplatinic acid as the catalyst [22, 24]. However, many problems were experienced at the start. It was more difficult than with terminally attached side chains to attain full substitution of the reactive Si-H sites on the polymer backbone with the laterally appended mesogenic units. This problem, obviously one of steric hindrance, was eventually overcome after a number of controlled experiments in which the use of the catalyst was optimised.

It was then suspected that, in the hydrosilylation process involving mesogenic units for lateral appendage, anomalous $\alpha$-addition of hydrogen at the double bond was occurring with hexachloroplatinic acid [26]. This was indeed confirmed to have taken place by $^1$H NMR spectroscopy, which showed the presence of the unwanted $\alpha$-form (Figure 2.3a). This was estimated to be contributing as much as 30% to the final SCLCP of the terminal cyano-substituted octyloxy series, and 5% in the case of the terminal alkyl/alkoxy-substituted series.

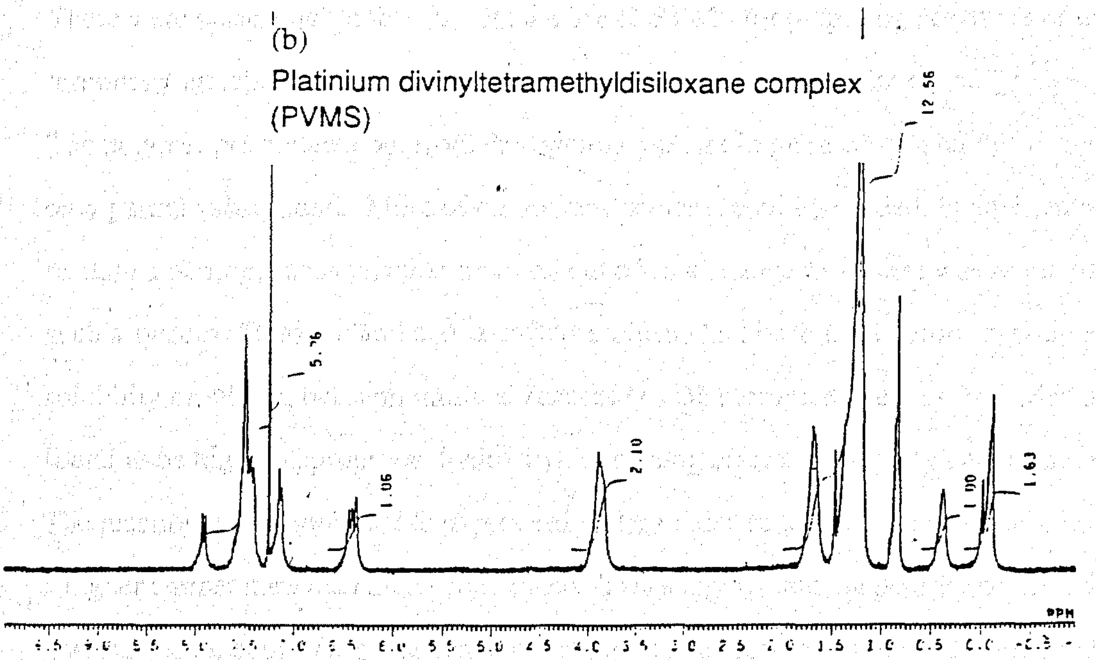
This brought about an urgent need to examine alternative catalysts to hexachloroplatinic acid. Various workers had used dicyclopentadienylplatinum (II) chloride [20], but this involved a laborious preparation of the catalyst which did not always give good yields or results. Following on the work of de Marignan *et al.* [26], platinum divinyltetramethyldisiloxane complex [27] (PVMS), made by Petrarch, was tried.
This worked very well; not only was a smaller concentration of catalyst required for the reaction, but also full substitution was effected at a much quicker rate. More importantly however, the reaction was able to proceed without the formation of anomalous products arising from $\alpha$-addition of hydrogen (Figure 2.3b). Furthermore as the catalyst could be used 'straight from the bottle', it did not have to be freshly prepared whenever it was needed or require stringent storage procedures, factors which had to be diligently

**Figure 2.3**

*Typical $^1H$ NMR spectra of laterally attached SCLCP prepared using two different catalysts, showing anomalous α-addition in the case of $H_2PtCl_6$*



(a)
Hexachloroplatinic Acid
($H_2PtCl_6$)



(b)
Platinium divinyltetramethyldisiloxane complex
(PVMS)

observed when dealing with hexachloroplatinic acid [28]. All subsequent hydrosilylations were performed using this new catalyst, PVMS.

The full repercussions of the use of PVMS are of course best seen from the results for polymers made using the two catalysts. The isotropisation temperatures of polymers synthesised with PVMS are as much as *ca.* 20 °C higher, a direct consequence of the prevention of anomalous addition (see Section 4.2.1 for a more detailed discussion). Although used largely for the laterally attached type of SCLCP, PVMS was also used to prepare conventional SCLCP with terminally attached mesogenic units. These hydrosilylations worked equally well, and polymer preparations made using the two catalysts gave virtually identical phase transition temperatures (see Section 4.2.4). This result reinforces the point that anomalous addition has not been observed for terminally attached polymers, and that the presence of these unwanted products accounts for the suppression of the transition temperatures for laterally attached polymers made using hexachloroplatinic acid.

There were occasional problems with the use of PVMS for preparing polymers of the terminally attached type, and these arose with some side chains with cyano-groups. The polymer precipitated out from the reaction mixture in these cases, and this occurred at only partial substitution. More of the solvent, toluene, could be added, in an attempt to reattain a homogeneous reaction mixture, but often a change in solvent was required for such a system. Benzene and $\alpha,\alpha,\alpha$-trifluorotoluene had been used before to counter solubility problems, but with minimal success [17]. Dichloromethane was then tried and found to be highly appropriate, hydrosilylation being effected smoothly under reflux. The reaction was therefore able to proceed under milder conditions, since toluene boils at a higher temperature than dichloromethane. This suggests that the polarity of the solvent governs the kinetics of the reaction and plays a more important role than the temperature of the reaction mixture. In fact, the reaction does proceed at room temperature in dichloromethane. However, in the case of a sterically hindered laterally attached side chain, the reaction took a week, during which monitoring and further catalyst additions were carried out, before substitution was ascertained to be complete [29]. An important consideration concerning the use of dichloromethane was to determine that the change in solvent had not affected the phase transition temperatures of the SCLCP. This was checked and found to be within acceptable limits for a pair of polymers synthesised using not only different solvents, but also the different catalysts (see Section 4.2.4).

The reason behind the precipitation of these polymers from the reaction mixture is presumed to be a molecular weight effect, since it was observed to take place with a few terminally attached side chains of quite high molar mass. Alternatively of course, it could be due to diminished solubility stemming from steric crowding with the higher molar mass side chains, for the problem was alleviated when these side chains were appended on the copolymer backbone, where not every adjacent silicon atom is required to carry a bulky mesogenic group. Where cyano-groups are present, cross-linking is always a threat through hydrosilylation both at the alkene and nitrile functions [30], and its occurrence would perhaps not be too surprising when one considers that PVMS is structurally related to known cross-linking agents. The reactivity and concentration of PVMS can be reduced in these circumstances, by diluting one part of catalyst to five parts of dry dichloromethane [31]. However, precipitation of the polymer was avoided, and much cleaner products were obtained as a result of changing the solvent used in these hydrosilylation reactions from toluene to dichloromethane, so it seems certain that the problem was simply one of solubility.

### 2.2.5 Purification

In a phase study in which liquid crystalline side chain polymers are mixed with low molar mass liquid crystal materials of similar structure [32], it has been shown that mere traces of low molar mass compounds strongly affect the properties of the LCP. This is manifested by a reduction in the glass transition temperature of the polymer, change in the isotropisation temperature, and/or a broadening of the mesophase transition(s). Hence it is important that the resultant LC polymers are not 'contaminated' by unreacted side chain precursor, and that its removal is complete in order that the 'true' thermal behaviour of the polymer may be distinguished. This is achieved by a series of precipitations with methanol. Alternative methods of purification are by preparative gel permeation chromatography [33] or Soxhlet extraction [34].

Phase transition temperatures are found to be variable depending on whether only two or three precipitations have been performed [20, 35, 36] or a larger number [26, 37]. This has been shown by Nestor *et al.* to be due simply to the fact that three precipitations or less are frequently insufficient to eradicate the alkene completely from the SCLCP. With a larger number of precipitations, the resultant polymers are found to be free from side chain precursor, and to have higher glass transition and clearing temperatures [24]. These results are therefore consistent with those reported by Finkelmann *et al.* for mixtures of polymeric and low molar mass materials [32]. The DSC peak widths, or biphasic regions, are narrowed as well, consistent with a reduction in the amounts of low molar mass compounds present and confirming removal of side chain precursor. Consequently, it could not be assumed that some arbitrary number of precipitations would be sufficient for purification, since different alkenes possess different degrees of solubility in methanol. The removal of side chain precursor has therefore to be monitored carefully in every case through the use of thin layer chromatography on silica with an appropriate eluent (TLC -- single spot, polymer $R_f = 0$, alkene $R_f$ variable and dependent on eluent system used) [33]. Detection is possible even down to 0.06% of side chain precursor, when tested in controlled exercises [24].

The precipitation process was carried out by dissolving the crude polymer in the minimum volume of dichloromethane, followed by the addition of approximately four times this volume of methanol. The mixture of precipitated polymer and cloudy supernatant emulsion was centrifuged for half an hour (4 500 r.p.m.), whereon the supernatant liquid was decanted off and the polymer redissolved in dichloromethane. The precipitations were repeated until a pure product, free from any detectable concentration of side chain precursor (TLC), was obtained.

The solvents used in the precipitations had to be thoroughly dry, otherwise emulsification persists and the polymer is poorly padded down at the end of the centrifugation. Furthermore, purification with 'wet' solvents is made inefficient by loss of polymer when decanting off the supernatant liquid. These problems were avoided by using methanol and dichloromethane both of which had been dried overnight over molecular sieves prior to its use.

## 2.3 REFERENCES

1. F. Hessel and H. Finkelmann, *Polym. Bull. (Berlin)*, **14**, 375 (1985).
2. P. Keller, F. Hardouin, M. Mauzac and M.F. Achard, *Mol. Cryst. Liq. Cryst.*, **155**, 171 (1988).
3. D. Coates and G.W. Gray, *J. Chem. Soc., Perkin Trans. II*, **7**, 863 (1979).
4. A. Hassner and V. Alexanian, *Tetrahedron Lett.*, 4475 (1978).
5. E. Haslam, *Tetrahedron*, **36**, 2409 (1980).
6. B. Neises and W. Steglich, *Angew. Chem. Int. Ed. Engl.*, **17**, 522 (1978).
7. K.J. Toyne, in *"Thermotropic Liquid Crystals"* (ed. G.W. Gray), CRAC Series, Vol. 22, John Wiley and Sons, Chichester (1987).
8. O. Mitsunobu, *Synthesis*, 1 (1981).
9. G.W. Gray, J.B. Hartley and B. Jones, *J. Chem. Soc.*, 1412 (1955).
10. W.C. Frank, Y.C. Kim and R.F. Heck, *J. Org. Chem.*, **43**, 2947 (1978).
11. B.A. Patel and R.F. Heck, *J. Org. Chem.*, **43**, 3898 (1978).
12. D. Papa, E. Schwenk and H. Hankin, *J. Am. Chem. Soc.*, **69**, 3018 (1947).
13. L.F. Fieser and C.K. Bradsher, *J. Am. Chem. Soc.*, **58**, 1738 (1936).
14. C.T. West, S.J. Donnelly, D.A. Kooistra and M.P. Doyle, *J. Org. Chem.*, **38**, 2675 (1973).
15. H. Niwa, T. Hida and K. Yamada, *Tetrahedron Lett.*, **22**, 4239 (1981).
16. H. Ringsdorf and A. Schneller, *Makromol. Chem., Rapid Commun.*, **3**, 557 (1982).
17. G. Nestor, Ph.D. Thesis, Univeristy of Hull (1988).
18. S. Takenaka, H. Morita, S. Kusabayashi, Y. Masuda, M. Iwano and T. Ikemoto, *Chem. Lett.*, 1559 (1988).
19. W.D. Hawthorne, Ph.D. Thesis, University of York (1986).
20. M.A. Apfel, H. Finkelmann, G.M. Janini, R.J. Laub, B.H. Luhman, A. Price, W.L. Roberts, T.J. Shaw and C.A. Smith, *Anal. Chem.*, **57**, 651 (1985).
21. H. Stevens, G. Rehage and H. Finkelmann, *Macromolecules*, **17**, 851 (1984).
22. P.A. Gemmell, G.W. Gray and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **122**, 205 (1985).
23. G.W. Gray, in *"Side Chain Liquid Crystal Polymers"* (ed. C.B. McArdle), Blackie, Glasgow (1989).

24. G. Nestor, M.S. White, G.W. Gray, D. Lacey and K.J. Toyne, *Makromol. Chem.*, **188**, 2759 (1987).

25. M.S. White, unpublished results.

26. G. de Marignan, D. Teyssie, S. Boileau, J. Malthète and C. Noel, *Polymer*, **29**, 1318 (1988).

27. B.D. Karstedt, U.S. Patent 3 775 452 (1973).

28. G.W. Gray, D. Lacey, G. Nestor and M.S. White, *Makromol. Chem., Rapid Commun.*, **7**, 71 (1986).

29. R.A. Lewthwaite, unpublished results.

30. H. Finkelmann, U. Kiechle and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **94**, 343 (1983).

31. S. Takikawa, personal communication.

32. H. Finkelmann, H.J. Kock and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **89**, 23 (1982).

33. W. Kreuder and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, **4**, 807 (1983).

34. H. Finkelmann, H.J. Kock and G. Rehage, *Makromol. Chem., Rapid Commun.*, **2**, 317 (1981).

35. B.A. Jones, J.S. Bradshaw, M. Nishioka and M.L. Lee, *J. Org. Chem.*, **49**, 4947 (1984).

36. M. Mauzac, F. Hardouin, H. Richard, M.F. Achard, G. Sigaud and H. Gasparoux, *Eur. Polym. J.*, **22**, 131 (1986).

37. K.E. Markides, M. Nishioka, B.J. Tarbet, J.S. Bradshaw and M.L. Lee, *Anal. Chem.*, **57**, 1296 (1985).

## three

# experimental

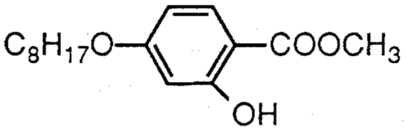
# 3.1 MESOGENIC SIDE CHAINS

## 3.1.1 Scheme A -

## Synthesis of 4-substituted biphenyl-4'-yl 2-(ω-alkenyloxy)-4-alkoxybenzoates

Experimental details are given only for the octyloxy compounds. The methoxy compounds were prepared similarly; their melting points and spectral data are recorded below each preparative method.

*Methyl 2-hydroxy-4-octyloxybenzoate (1)*



Methyl 2, 4-dihydroxybenzoate (33.60 g, 0.20 mol), 1-bromo-octane (46.35 g, 0.24 mol) and anhydrous potassium carbonate (138.0 g, 1.0 mol) in dry butanone (400 ml) were stirred together and heated under reflux, with the exclusion of moisture, until completion of the reaction (TLC). The potassium carbonate was filtered off, washed with butanone, and the crude product isolated from the filtrate was recrystallised several times from methanol to afford the pure ester as white crystals.
(Methyl 2-hydroxy-4-methoxybenzoate is available commercially from Aldrich)

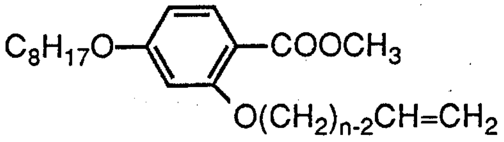
**1** : Yield: 40%; m.p. 46.5 - 47.5 °C.

MS (m/z) 280 ($M^+$), 168, 136.

$^1$H NMR ($CDCl_3$) δ 0.9 (3H, t, $CH_3$), 1.25 - 1.55 (10H, m, alkyl), 1.78 (2H, m, alkyl), 3.9 (3H, s, $CH_3O$), 3.97 (2H, t, $CH_2O$), 6.4 (1H, s, aromatic), 6.43 (1H, d, aromatic), 7.73 (1H, d, aromatic), 10.95 (1H, s, OH).

IR (KCl) vmax $cm^{-1}$ 3220 (O-H), 1680 (C=O), 1250, 1140 (C-O).

*Methyl 2-(ω-alkenyloxy)-4-octyloxybenzoates (2)*



Methyl 2-hydroxy-4-octyloxybenzoate (11.20 g, 0.04 mol), the appropriate alkenyl bromide (0.05 mol) and anhydrous potassium carbonate (33.12 g, 0.24 mol) in dry butanone (200 ml) were stirred together, with the exclusion of moisture, and heated under reflux until completion of reaction (TLC). The reaction mixture was poured into water (200 ml) and ethyl acetate (200 ml) was added. The organic layer was separated off and then shaken with 5% aqueous sodium hydroxide (200 ml) and finally with water (2 x 200 ml). The extract was dried ($MgSO_4$) and the solvent distilled off under reduced pressure to leave a yellow oil. Yields in excess of 95% were normally obtained and the products were pure enough to use in the subsequent hydrolysis step.

(The 4-methoxy analogues were also oils)

**2a** : n = 5

MS (m/z) 348 ($M^+$), 280.

$^1$H NMR* ($CDCl_3$) δ 0.88 (3H, t, $CH_3$), 1.2 - 1.55 (10H, m, alkyl), 1.9, 2.05, 2.27 (2H, m, alkyl), 3.85 (3H, s, $CH_3O$), 4.0 (4H, m, $CH_2O$), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.42 (1H, s, aromatic), 6.48 (1H, d, aromatic), 7.82 (1H, d, aromatic).

IR (Film) νmax $cm^{-1}$ 1740 (C=O), 1620 (C=C), 1260 - 1280, 1200 (C-O).

**2b** : n = 6

MS (m/z) 362 ($M^+$), 280.

*4-Methoxy analogues:*

**2ma** : n = 5

MS (m/z) 250 ($M^+$), 182, 150.

$^1$H NMR* ($CDCl_3$) δ 1.94, 2.3 (2H, m, alkyl), 3.82 (3H, s, $CH_3O$), 3.87 (3H, s, $CH_3O$), 4.02 (2H, t,

---

* Data specific to 5-spacer compound. NMR and IR spectra for **2a** and **2ma** were representative of those for **2b** and **2mb** respectively.

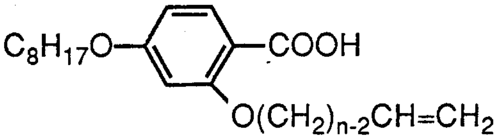
CH$_2$O), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.42 (1H, s, aromatic), 6.48 (1H, d, aromatic), 7.84 (1H, d, aromatic).

IR (Film) vmax cm$^{-1}$ 1730 (C=O), 1620 (C=C), 1260 - 1280, 1205 (C-O).

**2mb** : n = 6

MS (m/z) 264 (M$^+$), 182, 150.

*2-(ω-Alkenyloxy)-4-octyloxybenzoic acids (3)*



Sodium hydroxide pellets (8.0 g, 0.20 mol) were dissolved in a heated mixture of methanol (300 ml) and water (30 ml). The appropriate methyl 2-(ω-alkenyloxy)-4-octyloxybenzoate (0.04 mol) was added and the resultant mixture heated under reflux for 2 hours. The methanol was removed under reduced pressure and water (200 ml) was added to dissolve the white residue. Acidification (Congo Red) with concentrated hydrochloric acid gave a white precipitate which was extracted into chloroform (3 x 200 ml). The extracts were washed with saturated brine (2 x 300 ml) and dried (MgSO$_4$). The chloroform was removed under reduced pressure and the product crystallised from petroleum fraction [bp 40-60 °C] to afford the acids as white powders.

**3a** : n = 5, Yield: 81%; m.p. 68.5 - 69.5 °C.

MS (m/z) 334 (M$^+$), 266.

$^1$H NMR* (CDCl$_3$) $\delta$ 0.9 (3H, t, CH$_3$), 1.2 - 1.6 (10H, m, alkyl), 1.8, 2.03, 2.26 (2H, m, alkyl), 4.0, 4.2 (2H, t, CH$_2$O), 5.06 (2H, m, alkene), 5.85 (1H, m, alkene), 6.5 (1H, s, aromatic), 6.62 (1H, d, aromatic), 8.13 (1H, d, aromatic), 10.7 (1H, s, COOH).

IR (KCl) vmax cm$^{-1}$ 2600 - 3200 (O-H), 1690 (C=O), 1620 (C=C), 1240 - 1270, 1205 (C-O).

**3b** : n = 6, Yield: 75%; m.p. 46.2 - 47.2 °C.

MS (m/z) 348 (M$^+$), 266.

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* Data specific to 5-spacer compound. NMR and IR spectra for **3a** and **3ma** were representative of those for **3b** and **3mb** respectively.

*4-Methoxy analogues:*

**3ma** : n = 5, Yield: 63%; m.p. 54.8 - 55.8 °C.

MS (m/z) 236 ($M^+$), 168, 150.

$^1$H NMR* ($CDCl_3$) δ 2.03, 2.25 (2H, m, alkyl), 3.87 (3H, s, $CH_3O$), 4.2 (2H, t, $CH_2O$), 5.05 (2H, m, alkene), 5.82 (1H, m, alkene), 6.5 (1H, s, aromatic), 6.65 (1H, d, aromatic), 8.15 (1H, d, aromatic), 10.7 (1H, s, COOH).

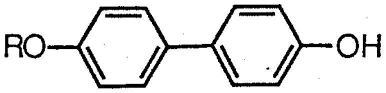
IR (KCl) vmax $cm^{-1}$ 3280 (O-H, intermolecularly H-bonded), 2600 - 3200 (O-H), 1730 (C=O), 1620 (C=C), 1240 - 1270 (C-O).

**3mb** : n = 6, Yield: 78%; m.p. 36.2 - 37.2 °C.

MS (m/z) 250 ($M^+$), 168, 150.

*Substituted phenols (4)*

The following 4-alkoxy-4'-hydroxybiphenyls **(4e - q)** were synthesised by selectively alkylating 4, 4'-biphenol (see Scheme Ai).



A solution of diethyl azodicarboxylate (4.18 g, 0.024 mol) in dry tetrahydrofuran (30 ml) was added dropwise with stirring over a period of one hour to a mixture of 4, 4'-biphenol (5.59 g, 0.03 mol), triphenylphosphine (6.30 g, 0.024 mol) and the appropriate alcohol (0.02 mol) in dry tetrahydrofuran (100 ml). Stirring was continued overnight at room temperature under anhydrous conditions. The precipitate of triphenylphosphine oxide was filtered off and the solvent was removed under reduced pressure. The solid residue was left to stir in diethyl ether for 2 hours and the remaining precipitate was filtered off and discarded. This procedure was then repeated on the solute using dichloromethane. The product was isolated by column chromatography (silica gel), eluting with dichloromethane. Crystallisation was performed from ethanol:water to afford the colourless products.

**4e** : R = $CH_3$, Yield: 30%; m.p. 182.7 - 183.7 °C.

MS (m/z) 200 $(M^+)$, 186.

$^1H$ NMR ($CDCl_3$) $\delta$ 3.85 (3H, s, $CH_3O$), 4.8 (1H, s, OH), 6.92, 7.42 (4H, q, aromatic).

IR (KCl) vmax cm$^{-1}$ 3400 (O-H), 2815 (C-H), 1610, 1505 (C=C), 1250 (C-O), 820 (1, 4 disub).

**4f** : R = $C_2H_5$, Yield: 32%; m.p. 167.2 - 168.2 °C.

MS (m/z) 214 $(M^+)$, 186.

$^1H$ NMR ($CDCl_3$) $\delta$ 1.45 (3H, t, $CH_3$), 4.08 (2H, t, $CH_2O$), 4.8 (1H, s, OH), 6.92, 7.42 (4H, q, aromatic).

IR (KCl) vmax cm$^{-1}$ 3400 (O-H), 1610, 1505 (C=C), 1250 (C-O), 820 (1, 4 disub).

**4g** : R = $C_3H_7$, Yield: 40%; m.p. 173.8 - 174.8 °C.

MS (m/z) 228 $(M^+)$, 186.

$^1H$ NMR ($CDCl_3$) $\delta$ 1.05 (3H, t, $CH_3$), 1.84 (2H, q, alkyl), 4.0 (2H, t, $CH_2O$), 4.8 (1H, s, OH), 6.92, 7.42 (4H, q, aromatic).

**4h** : R = $C_4H_9$, Yield: 41%; m.p. 169.4 - 170.4 °C.

MS (m/z) 242 $(M^+)$, 186.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.95 (3H, t, $CH_3$), 1.53 (2H, m, alkyl), 1.8 (2H, m, alkyl), 4.0 (2H, t, $CH_2O$), 4.8 (1H, s, OH), 6.92, 7.42 (4H, q, aromatic).

**4i** : R = $C_5H_{11}$, Yield: 45%; m.p. 159.2 - 160.2 °C.

MS (m/z) 256 $(M^+)$, 186.

$^1H$ NMR‡ ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 1.3 - 1.62 (4H, m, alkyl), 1.8 (2H, m, alkyl), 4.0 (2H, t, $CH_2O$), 4.66 (1H, s, OH), 6.92, 7.42 (4H, q, aromatic).

**4j** : R = $C_6H_{13}$, Yield: 41%; m.p. 157.5 - 158.5 °C.

MS (m/z) 270 $(M^+)$, 186.

**4k** : R = $C_7H_{15}$, Yield: 28%; m.p. 155.0 - 156.0 °C.

MS (m/z) 284 $(M^+)$, 186.

**4l** : R = $C_8H_{17}$, Yield: 52%; m.p. 153.5 - 154.5 °C.

MS (m/z) 298 $(M^+)$, 186.

**4m**: R = $C_9H_{19}$, Yield: 35%; m.p. 151.0 - 152.0 °C.

MS (m/z) 312 $(M^+)$, 186.

---

IR spectrum for **4f** was representative of those for **4g - p**.

‡ Data specific to pentyloxy compound. NMR spectrum for **4i** was representative of those for **4j - n**.

**4n** : R = $C_{10}H_{21}$, Yield: 36%; m.p. 149.5 - 150.5 °C.

MS (m/z) 326 ($M^+$), 186.

**4o** : R = $CH_2CH(CH_3)C_2H_5$, Yield: 21%; m.p. 134.5 - 135.5 °C.

MS (m/z) 256 ($M^+$), 186.

$^1$H NMR ($CDCl_3$) δ 0.96 (3H, t, $CH_3$), 1.03 (3H, d, $CH_3$), 1.3 (2H, m, alkyl), 1.9 (1H, m, alkyl), 3.8 (2H, m, $CH_2O$), 4.66 (1H, s, OH), 6.92, 7.42 (4H, q, aromatic).

**4p** : R = $CH(CH_3)C_6H_{13}$, Yield: 42%; m.p. 102.7 - 103.7 °C.

MS (m/z) 298 ($M^+$), 186.

$^1$H NMR ($CDCl_3$) δ 0.9 (3H, t, $CH_3$), 1.2 - 1.8 (13H, m, alkyl), 4.38 (1H, m, ArOCH), 4.72 (1H, s, OH), 6.88, 6.94, 7.44, 7.46 (2H, d, aromatic).

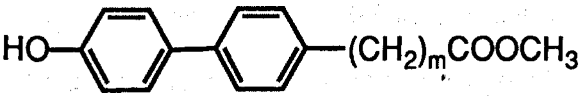
**4q** : R = $CH(CH_3)COOC_2H_5$, Yield: 23%; m.p. 117.5 - 118.5 °C.

MS (m/z) 286 ($M^+$), 213, 186.

$^1$H NMR ($CDCl_3$) δ 1.25 (3H, t, $CH_3$), 1.63 (3H, d, $CH_3$), 4.25 (2H, q, $CH_2O$), 4.72 (1H, q, ArOCH), 4.8 (1H, s, OH), 6.92, 7.42 (4H, q, aromatic).

IR (KCl) νmax cm$^{-1}$ 3400 (O-H), 1725 (C=O), 1610, 1505 (C=C), 1250 (C-O), 820 (1, 4 disub).

Three 4'-substituted-4-hydroxybiphenyls (**4r - t**) were synthesised by esterifying the acids 4-hydroxybiphenyl-4'-carboxylic acid, 2-(4-hydroxybiphenyl-4'-yl)ethanoic acid and 3-(4-hydroxybiphenyl-4'-yl)propanoic acid (see Scheme Aii).



A few drops of concentrated sulphuric acid were added to a solution of the appropriate carboxylic acid (0.01 mol) in methanol (100 ml) and the solution was boiled until the reaction was complete (TLC). The solvent was distilled off under reduced pressure and the white residue was dissolved in dichloromethane (100 ml). This solution was washed with saturated sodium bicarbonate (2 x 75 ml), water (3 x 100 ml) and dried ($MgSO_4$). Removal of the solvent, followed by crystallisation of the residue from methanol:water, yielded the esters as white powders.

**4r** : m = 0, Yield: 76%; m.p. 227.5 - 228.5 °C.

MS (m/z) 228 ($M^+$), 197.

$^1$H NMR ($CDCl_3$) δ 3.94 (3H, s, $CH_3O$), 4.93 (1H, s, OH), 6.92, 7.53, 7.56, 8.07 (2H, d, aromatic).

IR (KCl) νmax $cm^{-1}$ 3400 (O-H), 1740 (C=O), 1270, 1200 (C-O), 820 (1, 4 disub).

**4s** : m = 1, Yield: 75%; m.p. 104.2 - 105.2 °C.

MS (m/z) 242 ($M^+$), 183.

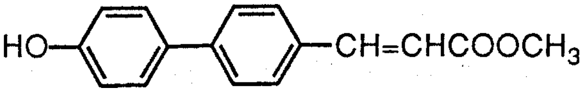
$^1$H NMR ($CDCl_3$) δ 3.67 (2H, s, $ArCH_2$), 3.72 (3H, s, $CH_3O$), 4.84 (1H, s, OH), 6.88, 7.32 (2H, d, aromatic), 7.47 (4H, m, aromatic).

**4t** : m = 2, Yield: 33%; m.p. 134.0 - 135.0 °C.

MS (m/z) 256 ($M^+$), 196, 183.

$^1$H NMR ($CDCl_3$) δ 2.66 (2H, t, alkyl), 2.98 (2H, t, $ArCH_2$), 3.68 (3H, s, $CH_3O$), 4.75 (1H, s, OH), 6.88, 7.24 (2H, d, aromatic), 7.44 (4H, m, aromatic).

Methyl 3-(4-hydroxybiphenyl-4'-yl)acrylate (**4u**) was prepared as illustrated by Scheme Aiii and described below:



Methyl acrylate (3.44 g, 0.04 mol) was added to a solution of 4-bromo-4'-hydroxybiphenyl (5.0 g, 0.02 mol), triethylamine (4.04 g, 0.04 mol), palladium (II) acetate (0.05 g, $2.2 \times 10^{-4}$ mol) and tri-*o*-tolylphosphine (0.20 g, $6.6 \times 10^{-4}$ mol) in dry acetonitrile and this was refluxed under nitrogen until completion of the reaction (TLC). The reaction mixture was then cooled in ice and diluted with acetone (50 ml).

The inorganic residue was filtered off and washed with acetone (2 x 50 ml).

The combined organic filtrates were distilled under reduced pressure to remove solvents and the residual product was crystallised from acetonitrile to give pale-yellow crystals.

**4u** : Yield: 37%; m.p. 229.0 - 230.0 °C.

MS (m/z) 254 ($M^+$), 223, 165.

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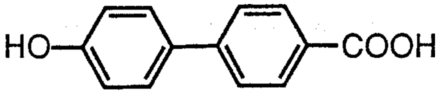
IR spectrum for **4r** was representative of those for **4s** and **4t**.

$^1H$ NMR ($CDCl_3$) δ 3.8 (3H, s, $CH_3O$), 4.7 (1H, s, OH), 6.46 (1H, d, alkene), 6.94, 7.47 (2H, d, aromatic), 7.52 (4H, m, aromatic), 7.7 (1H, d, ArCH=CH).

IR (KCl) νmax $cm^{-1}$ 3400 (O-H), 1745 (C=O), 1635, 1600 (C=C), 1285, 1175 - 1200 (C-O), 820 (1, 4 disub).

2-Methylbutyl 4-hydroxybiphenyl-4'-carboxylate (**4w**) was prepared by esterifying the acid (**A1**) derived as discussed below (see Scheme Aiv):

*4-Hydroxybiphenyl-4'-carboxylic acid (A1)*



A solution of 4-cyano-4'-hydroxybiphenyl (20.0 g, 0.10 mol) in a 1:1 (v:v) mixture of glacial acetic acid:50% aqueous sulphuric acid (200 ml) was boiled for 20 hours. The solvents were removed under reduced pressure and the product was crystallised from ethanol:water to afford a white powder.

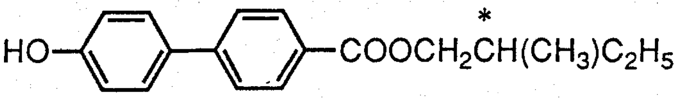
**A1** : Yield: 85%; m.p. 295.0 - 296.0 °C.

MS (m/z) 214 ($M^+$), 197.

$^1H$ NMR ($CDCl_3$) δ 4.7 (1H, s, OH), 6.94, 7.5, 7.6, 8.05 (2H, d, aromatic), 9.15 (1H, s, COOH).

IR (KCl) νmax $cm^{-1}$ 2500 - 3400 (O-H), 1680 (C=O), 1605 (C=C), 1250, 1200 (C-O), 940 (O-H), 830 (1, 4 disub).

*2-Methylbutyl 4-hydroxybiphenyl-4'-carboxylate (4w)*



A few drops of concentrated sulphuric acid were added to a solution of 4-hydroxybiphenyl-4'-carboxylic acid (10.70 g, 0.05 mol) and S(-)-2-methylbutan-1-ol (8.80 g, 0.10 mol) in dry toluene (300 ml), and the solution was boiled until the reaction was complete (TLC). The solvent was distilled off under reduced pressure and the oily residue was dissolved in dichloromethane (100 ml). This solution was washed with saturated sodium bicarbonate (2 x 100 ml), water (3 x 100 ml) and dried ($MgSO_4$). Crystallisation was performed from ethanol to yield the product as white crystals.

**4w** : Yield: 33%; m.p. 114.8 - 115.8 °C.

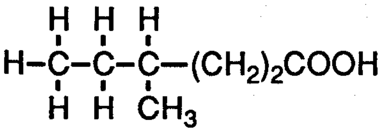
MS (m/z) 284 ($M^+$), 214, 197.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.9 - 1.05 (6H, m, $CH_3$), 1.4 (2H, m, alkyl), 1.87 (1H, m, alkyl), 4.2 (2H, m, $CH_2O$), 4.7 (1H, s, OH), 6.94, 7.5, 7.6, 8.05 (2H, d, aromatic).

IR (KCl) νmax $cm^{-1}$ 3400 (O-H), 1720 (C=O), 1610 (C=C), 1270 - 1290, 1190 (C-O).

Two branched 4-alkyl-4'-hydroxybiphenyls (**4x** and **y**) were synthesised by the following steps (see Scheme Av):

*4-Methylhexanoic acid (A2)*



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{CH_3}{C}}{-}(CH_2)_2COOH}$$

Super-dry ethanol (30 ml) was added carefully to sodium (1.15 g, 0.05 mol) at such a rate as to cause gentle reflux. On complete addition, the reaction mixture was heated for 30 minutes to ensure complete dissolution of the sodium. Diethyl malonate (8.80 g, 0.055 mol) was then added dropwise to the stirred solution, and the mixture was again heated for 30 minutes. 2-Methylbutyl bromide (6.85 g, 0.05 mol) was then added dropwise and the reaction mixture heated under reflux until the solution was found to be only weakly alkaline (pH 9). The ethanol was distilled off under reduced pressure; water (100 ml) was then added to the residue and the whole was shaken with diethyl ether (2 x 100 ml). The organic layer was separated, dried ($MgSO_4$), and the orange oil obtained on removal of the solvent was purified by distillation under reduced pressure.

The clear distillate was added dropwise to a hot, stirred solution of potassium hydroxide (15 g) in water (15 ml) and the mixture was boiled overnight. Complete hydrolysis was indicated by the miscibility of a sample of the mixture with water. The reaction mixture was diluted with water (200 ml) and the excess of ethanol was distilled off under reduced pressure. A 1:1 (v:v) mixture of concentrated hydrochloric acid:water (30 ml) was then added dropwise to the mixture which was allowed to boil for 24 hours and cooled. The product was extracted into diethyl ether (2 x 200 ml), and the combined extracts were washed with water (2 x 200 ml) and dried ($MgSO_4$). The residue obtained on removal of the solvent was purified by distillation under reduced pressure.

**A2** : Yield: 50%; b.p. 62 °C, 0.2 mm Hg.

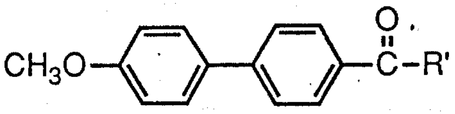
MS (m/z) 130 ($M^+$), 100.

$^1$H NMR ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 0.96 (3H, d, $CH_3$), 1.17 - 1.6 (4H, m, alkyl), 1.9 (1H, m, alkyl), 2.14, 2.35 (1H, q, alkyl), 11.45 (1H, s, COOH).

IR (Film) vmax cm$^{-1}$ 2700 - 3100 (O-H), 1710 (C=O), 940 (O-H).

3-Methylpentanoic acid was supplied by BDH Limited.

*4-Alkanoyl-4'-methoxybiphenyls (A3)*



The appropriate carboxylic acid (0.04 mol) was dissolved in thionyl chloride (50 ml) and boiled for 2 hours under anhydrous conditions. The crude acid chloride obtained on removal of the solvent was then added dropwise to a stirred, cooled (-10 °C) solution of ground aluminium chloride (6.40 g, 0.048 mol) and 4-methoxybiphenyl (7.36 g, 0.04 mol) in dry dichloromethane (100 ml). The mixture was allowed to warm up to room temperature with stirring which was continued for 12 hours. The reaction mixture was then poured onto ice and the organic material extracted into dichloromethane (2 x 200 ml). The combined extracts were washed with dilute sodium hydroxide (2 x 200 ml), water (3 x 200 ml) and dried ($MgSO_4$). The solvent was distilled off under reduced pressure and the product isolated by column chromatography, eluting with a 10:1 mixture of petroleum fraction [bp 40-60 °C]:diethyl ether. Crystallisation was performed from petroleum fraction [bp 40-60 °C] to afford the ketones as white powders.

**A3a** : R = $CH_2CH(CH_3)C_2H_5$, Yield: 54%; m.p. 100.5 - 101.5 °C.

MS (m/z) 282 ($M^+$), 226, 211.

$^1$H NMR ($CDCl_3$) δ 0.95 (3H, t, $CH_3$), 0.97 (3H, d, $CH_3$), 1.2 - 1.65 (2H, m, alkyl), 2.12 (1H, m, alkyl), 2.76, 2.98 (1H, q, $ArCOCH_2$), 3.85 (3H, s, $CH_3O$), 7.0, 7.58, 7.64, 8.02 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1680 (C=O), 1605 (C=C), 1260, 1200, 1040 (C-O), 815 (1, 4 disub).

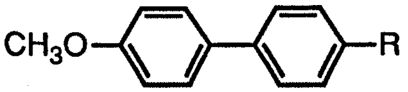
**A3b** : R = $(CH_2)_2CH(CH_3)C_2H_5$, Yield: 38%; m.p. 96.7 - 97.7 °C.

MS (m/z) 296 ($M^+$), 226, 211.

$^1$H NMR ($CDCl_3$) δ 0.95 (3H, t, $CH_3$), 0.97 (3H, d, $CH_3$), 1.2 - 1.65 (4H, m, alkyl), 1.8 (1H, m, alkyl), 3.0 (2H, m, $ArCOCH_2$), 3.85 (3H, s, $CH_3O$), 7.0, 7.58, 7.64, 8.02 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1680 (C=O), 1605 (C=C), 1260, 1200, 1040 (C-O), 815 (1, 4 disub).

### *4-Alkyl-4'-methoxybiphenyls (A4)*



Triethylsilane (1.28 g, 0.011 mol) was added dropwise to a stirred, cooled (0 °C) solution of the appropriate ketone (0.005 mol) in trifluoroacetic acid (30 ml).
The solution was allowed to warm up to room temperature with stirring which was continued until completion of the reaction (TLC). The mixture was then diluted with dichloromethane (50 ml) and carefully neutralised with saturated aqueous sodium bicarbonate. The organic layer was washed with water (2 x 100 ml), dried ($MgSO_4$) and the solvent distilled off under reduced pressure. The product was then purified by flash chromatography (silica gel), eluting the product with dichloromethane.

**A4a** : R = $(CH_2)_2CH(CH_3)C_2H_5$, Yield: 68%; m.p. 56.0 - 57.0 °C.

MS (m/z) 268 ($M^+$), 197.

$^1$H NMR ($CDCl_3$) δ 0.88 (3H, t, $CH_3$), 0.92 (3H, t, $CH_3$), 1.25, 1.4 (2H, m, alkyl), 1.64 (1H, m, alkyl), 2.63 (2H, m, $ArCH_2$), 3.85 (3H, s, $CH_3O$), 6.96, 7.24, 7.47, 7.53 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1505, 1250, 1080 (C-O), 820 (1, 4 disub), 745 ($[CH_2]_n$).

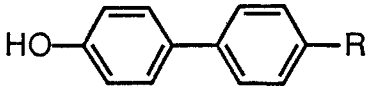
**A4b** : R = $(CH_2)_3CH(CH_3)C_2H_5$, Yield: 70%; m.p. 52.6 - 53.6 °C.

MS (m/z) 282 ($M^+$), 197.

$^1$H NMR ($CDCl_3$) δ 0.88 (6H, t, $CH_3$), 1.16, 1.37 (2H, m, alkyl), 1.64 (3H, m, alkyl), 2.63 (2H, t, $ArCH_2$), 3.85 (3H, s, $CH_3O$), 6.96, 7.24, 7.47, 7.53 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1505, 1250, 1080 (C-O), 820 (1, 4 disub), 745 ($[CH_2]_n$).

*4-Alkyl-4'-hydroxybiphenyls (4x and y)*



Boron tribromide (2 ml, 0.02 mol) was added carefully to a stirred, cooled (-70 °C) solution of the appropriate 4-alkyl-4'-methoxybiphenyl (0.05 mol) in dry dichloromethane. The mixture was allowed to warm up to room temperature, after which it was heated under reflux for 24 hours. Water (50 ml) was then carefully added to the solution with stirring and the mixture was shaken twice with diethyl ether (2 x 50 ml). The ethereal extracts were washed with saturated brine (2 x 100 ml), water (3 x 100 ml) and dried ($MgSO_4$). Crystallisation from ethanol:water afforded the products as fine light-brown crystals.

**4x** : R = $(CH_2)_2CH(CH_3)C_2H_5$, Yield: 60%; m.p. 121.5 - 122.5 °C.

MS (m/z) 254 ($M^+$), 183.

$^1$H NMR ($CDCl_3$) δ 0.9 (3H, t, $CH_3$), 0.95 (3H, d, $CH_3$), 1.23 (1H, m, alkyl), 1.45, 1.65 (2H, m, alkyl), 2.65 (2H, m, $ArCH_2$), 4.7 (1H, s, OH), 6.88, 7.23, 7.44, 7.46 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 3400 (O-H), 1610, 1505 (C=C), 1250 (C-O), 820 (1, 4 disub).

**4y** : R = $(CH_2)_3CH(CH_3)C_2H_5$, Yield: 85%; m.p. 117.8 - 118.8 °C.

MS (m/z) 268 ($M^+$), 183.

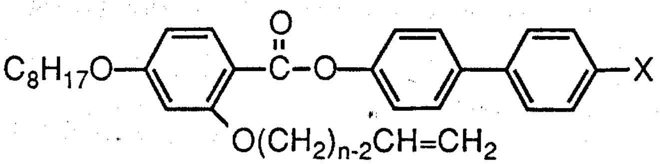
$^1$H NMR (CDCl$_3$) δ 0.88 (3H, t, CH$_3$), 0.92 (3H, d, CH$_3$), 1.17 (1H, m, alkyl), 1.35 (2H, m, alkyl), 1.6 (4H, m, alkyl), 2.6 (2H, t, ArCH$_2$), 4.75 (1H, s, OH), 6.92, 7.24, 7.44, 7.47 (2H, d, aromatic).

IR (KCl) νmax cm$^{-1}$ 3400 (O-H), 1610, 1505 (C=C), 1250 (C-O), 820 (1, 4 disub).

4-Cyano-4'-hydroxybiphenyl (**4a**), 4-hydroxy-4'-pentylbiphenyl (**4c**), 4-hydroxybiphenyl (**4z**), 4-fluoro-4'-hydroxybiphenyl (**4aa**), 4-hydroxy-4'-trifluoromethylbiphenyl (**4ab**), 4-bromo-4'-hydroxybiphenyl (**4ac**) and 4-hydroxy-4'-propylbiphenyl (**4ad**) were supplied by BDH Limited; 4-(*trans*-4-propylcyclohexyl)phenol (**4ae**) was supplied by E. Merck (Darmstadt).

Samples of methyl 3-(4-hydroxybiphenyl-4'-yl)butyrate (**4v**), 4-bromo-2'-fluoro-4'-hydroxybiphenyl (**4ai**) and 4-bromo-2-fluoro-4'-hydroxybiphenyl (**4aj**) were supplied by Dr L.K.M. Chan and of 6-cyano-2-napthol (**4af**), 4-cyano-3-fluoro-4'-hydroxybiphenyl (**4ag**), 4-cyano-3, 5-difluoro-4'-hydroxybiphenyl (**4ah**) by Dr M. Hird, both of the Hull University Liquid Crystal Group.

*4-Substituted biphenyl-4'-yl 2-(ω-alkenyloxy)-4-octyloxybenzoates (5)*



A mixture of the appropriate 2-(ω-alkenyloxy)-4-octyloxybenzoic acid (0.02 mol), the 4-substituted-4'-hydroxybiphenyl (0.02 mol), *N,N'*-dicyclohexylcarbodiimide (4.95 g, 0.024 mol) and 4-(*N*-pyrrolidino)pyridine (0.74 g, 0.005 mol) in dry dichloromethane (150 ml) was stirred overnight at room temperature with the exclusion of moisture. The substituted urea was filtered off and the product was purified by column chromatography (silica gel), eluting with a 4:1 mixture of dichloromethane:petroleum fraction [bp 40-60 °C]. Crystallisation from petroleum fraction [bp 40-60 °C]:toluene afforded the esters as white crystals.

**5a** : $n = 5$, $X = CN$, Yield: 65%; K 67.5 N (66.4) I.

MS (m/z) 511 ($M^+$), 317, 137.

$^1H$ NMR* ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 1.25 - 1.55 (10H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 4.05 (4H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.32 (2H, d, aromatic), 7.59 - 7.76 (6H, m, aromatic), 8.05 (1H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 2230 (C≡N), 1735 (C=O), 1600 (C=C), 1195 (C-O).

**5b** : $n = 6$, $X = CN$, Yield: 75%; K 74.5 N (58.2) I.

MS (m/z) 525 ($M^+$), 331, 137.

**5c** : $n = 5$, $X = C_5H_{11}$, Yield: 69%; K 44.5 N 50.2 I.

MS (m/z) 556 ($M^+$), 317, 137.

$^1H$ NMR* ($CDCl_3$) $\delta$ 0.9 (6H, t, $CH_3$), 1.25 - 1.85 (18H, m, alkyl), 1.95, 2.27 (2H, m, alkyl), 2.64 (2H, t, $ArCH_2$), 4.03 (4H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.53 (2H, m, aromatic), 7.25 (4H, d, aromatic), 7.5, 7.6 (2H, d, aromatic), 8.04 (1H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1740 (C=O), 1610 (C=C), 1200 (C-O).

**5d** : $n = 6$, $X = C_5H_{11}$, Yield: 52%; K 42.2 N 45.2 I.

MS (m/z) 570 ($M^+$), 331, 137.

**5e** : $n = 6$, $X = OCH_3$, Yield: 52%; K 102.2 N (□) I.

MS (m/z) 530 ($M^+$), 331.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 1.23 - 1.66 (12H, m, alkyl), 1.83 (4H, m, alkyl), 2.1 (2H, m, alkyl), 3.86 (3H, s, $CH_3O$), 4.03 (4H, m, $CH_2O$), 4.97 (2H, m, alkene), 5.78 (1H, m, alkene), 6.52 (2H, m, aromatic), 6.97, 7.24, 7.5, 7.56 (2H, d, aromatic), 8.04 (1H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1745 (C=O), 1610, 1500 (C=C), 1210 (C-O).

**5f** : $n = 6$, $X = OC_2H_5$, Yield: 55%; K 98.0 N (77.5) I.

MS (m/z) 544 ($M^+$), 331.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.9 (6H, m, $CH_3$), 1.23 - 1.66 (15H, m, alkyl), 1.83 (4H, m, alkyl), 2.1 (2H, m, alkyl), 4.03 (6H, m, $CH_2O$), 4.97 (2H, m, alkene), 5.78 (1H, m, alkene), 6.52 (2H, m, aromatic), 6.97, 7.24, 7.5, 7.56 (2H, d, aromatic), 8.04 (1H, d, aromatic).

**5g** : $n = 6$, $X = OC_3H_7$, Yield: 62%; K 89.2 N (51.4) I.

MS (m/z) 558 ($M^+$), 331.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.9, 1.05 (3H, t, $CH_3$), 1.23 - 1.66 (12H, m, alkyl), 1.83 (6H, m, alkyl),

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* Data specific to 5-spacer compound. NMR and IR spectra for **5a** and **5c** were representative of those for **5b** and **5d** respectively.

IR spectrum for **5e** was representative of those for **5f - p**.

□ Phase transition temperature difficult to determine due to fast recrystallisation.

2.1 (2H, m, alkyl), 4.03 (6H, m, $CH_2O$), 4.97 (2H, m, alkene), 5.78 (1H, m, alkene), 6.52 (2H, m, aromatic), 6.97, 7.24, 7.5, 7.56 (2H, d, aromatic), 8.04 (1H, d, aromatic).

**5h** : n = 6, X = $OC_4H_9$, Yield: 46%; K 80.8 N (74.0) I.

MS (m/z) 572 ($M^+$), 331.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.9, 1.0 (3H, t, $CH_3$), 1.23 - 1.66 (14H, m, alkyl), 1.83 (6H, m, alkyl), 2.1 (2H, m, alkyl), 4.03 (6H, m, $CH_2O$), 4.97 (2H, m, alkene), 5.78 (1H, m, alkene), 6.52 (2H, m, aromatic), 6.97, 7.24, 7.5, 7.56 (2H, d, aromatic), 8.04 (1H, d, aromatic).

**5i** : n = 6, X = $OC_5H_{11}$, Yield: 73%; K 75.0 N (65.5) I.

MS (m/z) 586 ($M^+$), 331.

$^1H$ NMR‡ ($CDCl_3$) $\delta$ 0.9 (6H, m, $CH_3$), 1.23 - 1.66 (18H, m, alkyl), 1.83 (4H, m, alkyl), 2.1 (2H, m, alkyl), 4.03 (6H, m, $CH_2O$), 4.97 (2H, m, alkene), 5.78 (1H, m, alkene), 6.52 (2H, m, aromatic), 6.97, 7.24, 7.5, 7.56 (2H, d, aromatic), 8.04 (1H, d, aromatic).

**5j** : n = 6, X = $OC_6H_{13}$, Yield: 50%; K 63.5 N 71.6 I.

MS (m/z) 600 ($M^+$), 331.

**5k** : n = 6, X = $OC_7H_{15}$, Yield: 68%; K 57.0 N 66.5 I.

MS (m/z) 614 ($M^+$), 331.

**5l** : n = 6, X = $OC_8H_{17}$, Yield: 61%; K 50.3 N 68.9 I.

MS (m/z) 628 ($M^+$), 331.

**5m** : n = 6, X = $OC_9H_{19}$, Yield: 53%; K 46.0 N 67.6 I.

MS (m/z) 642 ($M^+$), 331.

**5n** : n = 6, X = $OC_{10}H_{21}$, Yield: 53%; K 55.0 N 68.9 I.

MS (m/z) 656 ($M^+$), 331.

**5o** : n = 5, X = $OCH_2CH(CH_3)C_2H_5$, Yield: 68%; K 67.0 Ch (42.8) I.

MS (m/z) 572 ($M^+$), 317.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.85 - 1.08 (9H, m, $CH_3$), 1.23 - 1.65 (12H, m, alkyl), 1.75 - 2.0 (5H, m, alkyl), 2.28 (2H, m, alkyl), 3.84 (2H, m, $CH_2O$), 4.05 (4H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.83 (1H, m, alkene), 6.54 (2H, m, aromatic), 6.97, 7.27, 7.5, 7.56 (2H, d, aromatic), 8.04 (1H, d, aromatic).

$[\alpha]_D^{25}$ ($CHCl_3$) +5.0°.

**5p** : n = 5, X = $OCH(CH_3)C_6H_{13}$, Yield: 53%; K 36.8 Ch (5.7) I.

MS (m/z) 614 ($M^+$), 317.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.9 (6H, t, $CH_3$), 1.2 - 1.6 (23H, m, alkyl), 1.82, 1.94, 2.28 (2H, m, alkyl), 4.05 (4H, m, $CH_2O$), 4.38 (1H, m, ArOCH), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.54 (2H, m, aromatic), 6.95, 7.23, 7.5, 7.56 (2H, d, aromatic), 8.05 (1H, d, aromatic).

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‡ Data specific to pentyloxy compound. NMR spectrum for **5i** was representative of those for **5j** - **n**.

$[\alpha]_D^{25}$ ($CHCl_3$) -1.4°.

**5q** : n = 5, X = $OCH(CH_3)COOC_2H_5$, Yield: 70%; K 52.0 Ch (-5.0) I.

MS (m/z) 602 ($M^+$), 529, 317.

$^1$H NMR ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 1.25 - 1.65 (16H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 4.03 (4H, m, $CH_2O$), 4.25 (2H, q, $CH_2O$), 4.72 (1H, q, ArOCH), 4.97 (2H, m, alkene), 5.78 (1H, m, alkene), 6.52 (2H, m, aromatic), 6.97, 7.24, 7.5, 7.56 (2H, d, aromatic), 8.04 (1H, d, aromatic).

IR (KCl) vmax cm$^{-1}$ 1745, 1720 (C=O), 1610, 1500 (C=C), 1240 - 1270, 1210, 1130 (C-O).

$[\alpha]_D^{25}$ ($CHCl_3$) +12.5°.

**5r** : n = 5, X = $COOCH_3$, Yield: 58%; K 90.6 N (□) I.

MS (m/z) 544 ($M^+$), 513, 317.

$^1$H NMR ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 1.25 - 1.55 (10H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 3.94 (3H, s, $CH_3O$), 4.05 (4H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.53 (2H, m, aromatic), 7.3 (2H, d, aromatic), 7.65 (4H, d, aromatic), 8.06 (1H, d, aromatic), 8.12 (2H, d, aromatic).

IR (KCl) vmax cm$^{-1}$ 1740, 1720 (C=O), 1610 (C=C), 1275, 1190 (C-O).

**5s** : n = 5, X = $CH_2COOCH_3$, Yield: 63%; K 71.7 N (19.8) I.

MS (m/z) 558 ($M^+$), 499, 317.

$^1$H NMR ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 1.23 - 1.6 (10H, m, alkyl), 1.81, 1.94, 2.28 (2H, m, alkyl), 3.68 (2H, s, $ArCH_2CO$), 3.72 (3H, s, $CH_3O$), 4.04 (4H, m, $CH_2O$), 5.02 (2H, m, alkene), 5.82 (1H, m, alkene), 6.54 (2H, m, aromatic), 7.26, 7.35, 7.54, 7.6 (2H, d, aromatic), 8.05 (1H, d, aromatic).

IR (KCl) vmax cm$^{-1}$ 1740, 1720 (C=O), 1610 (C=C), 1270, 1190, 1160, 1140 (C-O).

**5t** : n = 5, X = $(CH_2)_2COOCH_3$, Yield: 59%; K 56.0 N (29.8) I.

MS (m/z) 572 ($M^+$), 541, 317.

$^1$H NMR ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 1.2 - 1.6 (10H, m, alkyl), 1.81, 1.94, 2.28 (2H, m, alkyl), 2.61 (2H, t, alkyl), 3.0 (2H, t, $ArCH_2$), 3.68 (3H, s, $CH_3O$), 4.04 (4H, m, $CH_2O$), 5.02 (2H, m, alkene), 5.82 (1H, m, alkene), 6.54 (2H, m, aromatic), 7.24, 7.27, 7.52, 7.59 (2H, d, aromatic), 8.04 (1H, d, aromatic).

IR (KCl) vmax cm$^{-1}$ 1740 (C=O), 1610 (C=C), 1190, 1150, 1050 (C-O).

**5u** : n = 5, X = $CH{=}CHCOOCH_3$, Yield: 57%; K 103.5 N 122.5 I.

MS (m/z) 570 ($M^+$), 317.

$^1$H NMR ($CDCl_3$) $\delta$ 0.9 (3H, t, $CH_3$), 1.25 - 1.55 (12H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 3.82 (3H, s, $CH_3O$), 4.03 (4H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.46 (1H, d, alkene), 6.52 (2H, m, aromatic), 7.32 (2H, d, aromatic), 7.56 - 7.65 (6H, m, aromatic), 7.7 (1H, d, ArCH=CH), 8.05 (1H, d, aromatic).

IR (KCl) vmax cm$^{-1}$ 1740, 1725 (C=O), 1635, 1610 (C=C), 1190, 1150 - 1170 (C-O).

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□ Phase transition temperature difficult to determine due to fast recrystallisation.

**5v** : n = 5, X = $CH(CH_3)CH_2COOCH_3$, Yield: 60%; K 54.5 I.

MS (m/z) 586 ($M^+$), 513, 317.

$^1H$ NMR ($CDCl_3$) δ 0.9 (3H, t, $CH_3$), 1.2 - 1.55 (14H, m, alkyl), 1.81, 1.94, 2.28 (2H, m, alkyl), 2.64 (2H, m, alkyl), 3.34 (1H, m, ArCH), 3.67 (3H, s, $CH_3O$), 4.05 (4H, m, $CH_2O$), 5.02 (2H, m, alkene), 5.82 (1H, m, alkene), 6.54 (2H, m, aromatic), 7.25, 7.3, 7.53, 7.6 (2H, d, aromatic), 8.05 (1H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1740, 1700 (C=O), 1610 (C=C), 1270, 1190, 1170, 1130 (C-O).

$[\alpha]_D^{25}$ ($CHCl_3$) -9.0°.

**5w** : n = 5, X = $COOCH_2CH(CH_3)C_2H_5$, Yield: 73%; K 63.4 Ch (32.6) I.

MS (m/z) 600 ($M^+$), 513, 317.

$^1H$ NMR ($CDCl_3$) δ 0.85 - 1.05 (9H, m, $CH_3$), 1.25 - 1.6 (13H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 4.05 (4H, m, $CH_2O$), 4.2 (2H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.53 (2H, m, aromatic), 7.3 (2H, d, aromatic), 7.65 (4H, d, aromatic), 8.06 (1H, d, aromatic), 8.12 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1740, 1720 (C=O), 1610 (C=C), 1185 - 1210, 1150 (C-O).

$[\alpha]_D^{25}$ ($CHCl_3$) +1.6°.

**5x** : n = 5, X = $(CH_2)_2CH(CH_3)C_2H_5$, Yield: 53%; K 44.4 Ch (32.6) I.

MS (m/z) 570 ($M^+$), 317.

$^1H$ NMR ($CDCl_3$) δ 0.85 - 0.95 (9H, m, $CH_3$), 1.25 - 1.6 (13H, m, alkyl), 1.65, 1.82, 1.95, 2.3 (2H, m, alkyl), 2.63 (2H, m, $ArCH_2$), 4.0, 4.05 (2H, t, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.25 (4H, d, aromatic), 7.5, 7.6 (2H, d, aromatic), 8.05 (1H, d, aromatic).

$[\alpha]_D^{25}$ ($CHCl_3$) +4.7°.

**5y** : n = 5, X = $(CH_2)_3CH(CH_3)C_2H_5$, Yield: 39%; K 41.3 Ch (32.2) I.

MS (m/z) 584 ($M^+$), 317.

$^1H$ NMR ($CDCl_3$) δ 0.85 - 0.95 (9H, m, $CH_3$), 1.25 - 1.6 (15H, m, alkyl), 1.65, 1.82, 1.95, 2.3 (2H, m, alkyl), 2.63 (2H, m, $ArCH_2$), 4.0, 4.05 (2H, t, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.25 (4H, d, aromatic), 7.5, 7.6 (2H, d, aromatic), 8.05 (1H, d, aromatic).

$[\alpha]_D^{25}$ ($CHCl_3$) +2.4°.

**5z** : n = 5, X = H, Yield: 52%; K 92.7 I.

MS (m/z) 486 ($M^+$), 317.

$^1H$ NMR ($CDCl_3$) δ 0.89 (3H, t, $CH_3$), 1.25 - 1.6 (10H, m, alkyl), 1.82, 1.96, 2.3 (2H, m, alkyl), 4.03 (4H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.25 (2H, d, aromatic), 7.36 (1H, d, aromatic), 7.45 (2H, m, aromatic), 7.58 (4H, m, aromatic), 8.05 (1H, d, aromatic).

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IR spectrum for **5c** was representative of those for **5x - z**.

**5aa** : $n = 5$, $X = F$, Yield: 72%; K 68.3 N (30.4) I.

MS (m/z) 504 ($M^+$), 317.

IR (KCl) νmax $cm^{-1}$ 1730 (C=O), 1615 (C=C), 1255, 1210, 1170, 1140 (C-O).

**5ab** : $n = 5$, $X = CF_3$, Yield: 64%; K 79.2 N (38.0) I.

MS (m/z) 554 ($M^+$), 317.

**5ac** : $n = 5$, $X = Br$, Yield: 38%; K 67.7 N (49.0) I.

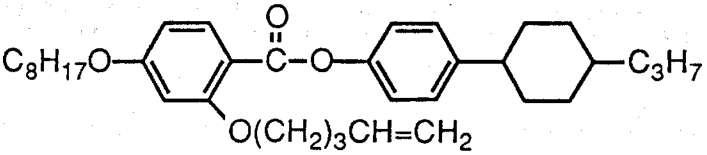
MS (m/z) 566 ($M^+$), 564 ($M^+$), 317.

**5ad** : $n = 5$, $X = C_3H_7$, Yield: 64%; K 57.5 N (50.3) I.

MS (m/z) 528 ($M^+$), 317.

$^1$H NMR ($CDCl_3$) δ 0.9, 0.97 (3H, t, $CH_3$), 1.25 - 1.55 (10H, m, alkyl), 1.68, 1.82, 1.94, 2.29 (2H, m, alkyl), 2.63 (2H, t, $ArCH_2$), 4.03 (4H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.24 (4H, d, aromatic), 7.5, 7.6 (2H, d, aromatic), 8.04 (1H, d, aromatic).

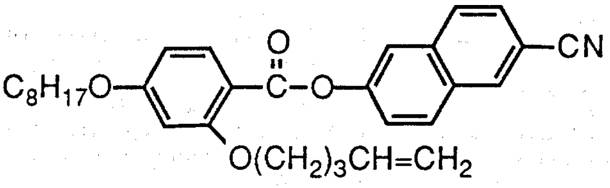
*Variations in mesogenic core:*



**5ae** : Yield: 62%; K 56.0 N (41.0) I.

MS (m/z) 532 ($M^+$), 317.

$^1$H NMR ($CDCl_3$) δ 0.9 (6H, t, $CH_3$), 1.07 (2H, m, alkyl), 1.2 - 1.55 (16H, m, alkyl), 1.75 - 1.95 (8H, m, alkyl), 2.27 (2H, m, alkyl), 4.04 (4H, m, $CH_2O$), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.09, 7.23 (2H, d, aromatic), 8.03 (1H, d, aromatic).



**5af** : Yield: 60%; K 61.2 N (-1.5) I.

MS (m/z) 509 ($M^+$), 317.

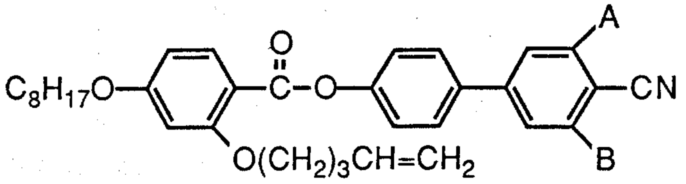
---

NMR spectrum for **5a** was representative of those for **5aa**, **5ab** and **5ac**.
IR spectrum for **5aa** was representative of those for **5ab** and **5ac**.

IR spectrum for **5c** was representative of those for **5ad** and **5ae**.

$^1$H NMR (CDCl$_3$) δ 0.9 (3H, t, CH$_3$), 1.25 - 1.55 (10H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 4.05 (4H, m, CH$_2$O), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.5, 7.64 (1H, d, aromatic), 7.75 (1H, s, aromatic), 7.9, 7.95, 8.08 (1H, d, aromatic), 8.25 (1H, s, aromatic).

IR (KCl) vmax cm$^{-1}$ 2230 (C≡N), 1720 (C=O), 1610 (C=C), 1250, 1210, 1140 (C-O).



**5ag** : A = F, B = H, Yield: 72%; K 67.5 N (39.8) I.

MS (m/z) 529 (M$^+$), 317.

$^1$H NMR (CDCl$_3$) δ 0.9 (3H, t, CH$_3$), 1.25 - 1.55 (10H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 4.05 (4H, m, CH$_2$O), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.32 (2H, d, aromatic), 7.48 (2H, m, aromatic), 7.58 - 7.73 (3H, m, aromatic), 8.05 (1H, d, aromatic).

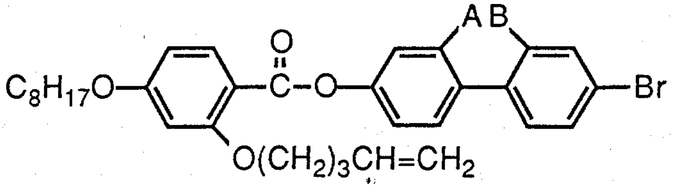
IR (KCl) vmax cm$^{-1}$ 2230 (C≡N), 1710 (C=O), 1610 (C=C), 1270, 1200, 1125 (C-O).

**5ah** : A = F, B = F, Yield: 61%; K 45.3 N (-1.7) I.

MS (m/z) 547 (M$^+$), 317.

$^1$H NMR (CDCl$_3$) δ 0.9 (3H, t, CH$_3$), 1.25 - 1.55 (10H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 4.05 (4H, m, CH$_2$O), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.26, 7.35, 7.6 (2H, d, aromatic), 8.04 (1H, d, aromatic).

IR (KCl) vmax cm$^{-1}$ 2230 (C≡N), 1730 (C=O), 1610 (C=C), 1200, 1170 (C-O).



**5ai** : A = F, B = H, Yield: 47%; K 52.7 N (12.2) I.

MS (m/z) 584 (M$^+$), 582 (M$^+$), 317.

$^1$H NMR (CDCl$_3$) δ 0.9 (3H, t, CH$_3$), 1.25 - 1.55 (10H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 4.05 (4H, m, CH$_2$O), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.07 (2H, m, aromatic), 7.42 (2H, d, aromatic), 7.57 (3H, m, aromatic), 8.05 (1H, d, aromatic).

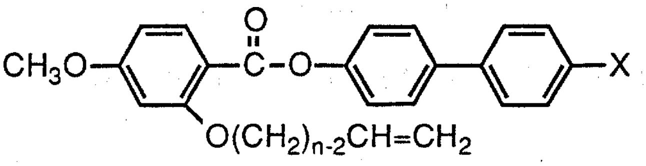
**5aj** : A = H, B = F, Yield: 39%; K 64.0 N (20.2) I.

MS (m/z) 584 (M$^+$), 582 (M$^+$), 317.

$^1$H NMR (CDCl$_3$) δ 0.9 (3H, t, CH$_3$), 1.25 - 1.55 (10H, m, alkyl), 1.82, 1.94, 2.3 (2H, m, alkyl), 4.05 (4H, m, CH$_2$O), 5.0 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (2H, m, aromatic), 7.25 - 7.43 (6H, m, aromatic), 7.56 (1H, d, aromatic), 8.05 (1H, d, aromatic).

IR spectrum for **5aa** was representative of those for **5ai** and **5aj**.

*4-Methoxy analogues of the 4-octyloxy compounds:*



**5ma:** n = 5, X = CN, Yield: 59%; K 92.8 N (49.3) I.

MS (m/z) 413 ($M^+$), 219, 150.

$^1$H NMR* ($CDCl_3$) δ 1.94, 2.3 (2H, m, alkyl), 3.87 (3H, s, $CH_3O$), 4.18 (2H, t, $CH_2O$), 5.02 (2H, m, alkene), 5.84 (1H, m, alkene), 6.54 (2H, m, aromatic), 7.32 (2H, d, aromatic), 7.59 - 7.76 (6H, m, aromatic), 8.07 (1H, d, aromatic).

IR (KCl) νmax cm$^{-1}$ 2230 (C≡N), 1715 (C=O), 1610 (C=C), 1275 (C-O).

**5mb:** n = 6, X = CN, Yield: 38%; K 110.0 N (33.5) I.

MS (m/z) 427 ($M^+$), 233, 150.

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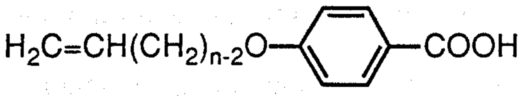
* Data specific to 5-spacer compound. NMR and IR spectra for **5ma** were representative of those for **5mb**.

## 3.1.2 Scheme B -

### Synthesis of 4-substituted phenyl 4-ω-alkenyloxybenzoates and 4-substituted biphenyl-4'-yl 4-ω-alkenyloxybenzoates

*4-ω-Alkenyloxybenzoic acids (6)*



To a stirred solution of potassium hydroxide (6.72 g, 0.12 mol) in a mixture of ethanol (80 ml) and water (10 ml) was added 4-hydroxybenzoic acid (6.90 g, 0.05 mol). A spatula full of potassium iodide was then added, followed by the dropwise addition of the alkenyl bromide (0.12 mol). The reaction mixture was boiled for 24 hours. A 10% potassium hydroxide solution (50 ml) was then added and the solution was heated for a further 4 hours. The reaction mixture was diluted with water (200 ml) and the product was precipitated on addition of concentrated hydrochloric acid. The crude material was filtered off and crystallised from ethanol:water to give white crystals.

**6a** : n = 5, Yield: 79%; K 123.0 N 152.0 I.

MS (m/z) 206 (M$^+$), 138, 121.

$^1$H NMR* (CDCl$_3$) δ 1.9 (2H, m, alkyl), 2.23 (2H, m, alkyl), 4.0 (2H, t, CH$_2$O), 5.02 (2H, m, alkene), 5.84 (1H, m, alkene), 6.9 (2H, d, aromatic), 8.0 (2H, d, aromatic).

IR (KCl) νmax cm$^{-1}$ 2550 - 3100 (O-H), 1680 (C=O), 1610 (C=C), 1260 (C-O), 920 - 955 (O-H), 850 (1, 4 disub).

**6b** : n = 6, Yield: 74%; K 101.0 N 140.0 I.

MS (m/z) 220 (M$^+$), 138, 121.

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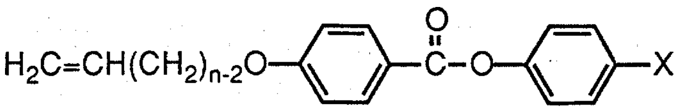
* Data specific to 5-spacer compound. NMR and IR spectra for **6a** were representative of those for **6b**.

### *4-Substituted phenyl 4-ω-alkenyloxybenzoates (7)*



A mixture of the appropriate 4-ω-alkenyloxybenzoic acid (0.01 mol), the 4-substituted phenol (0.01 mol), *N,N'*-dicyclohexylcarbodiimide (2.47 g, 0.012 mol) and 4-(*N*-pyrrolidino)pyridine (0.37 g, 2.5 x $10^{-3}$ mol) in dry dichloromethane (50 ml) was stirred overnight at room temperature with the exclusion of moisture. The substituted urea was filtered off and the product was purified by column chromatography (silica gel), eluting with a 4:1 mixture of dichloromethane:petroleum fraction [bp 40-60 °C]. Crystallisation from ethanol afforded the esters as white crystals.

**7a** : n = 5, X = CN, Yield: 75%; K 77.0 N 77.8 I.

MS (m/z) 307 ($M^+$), 189, 121.

$^1$H NMR$^*$ ($CDCl_3$) δ 1.94 (2H, m, alkyl), 2.26 (2H, m, alkyl), 4.06 (2H, t, $CH_2O$), 5.04 (2H, m, alkene), 5.86 (1H, m, alkene), 7.0, 7.35, 7.73, 8.13 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 2230 (C≡N), 1735 (C=O), 1600, 1510 (C=C), 1260, 1205, 1170, 1065 (C-O), 850 (1, 4 disub).

**7b** : n = 6, X = CN, Yield: 79%; K 63.0 N (62.8) I.

MS (m/z) 321 ($M^+$), 203, 121.

**7c** : n = 6, X = $(CH_2)_2CH(CH_3)C_2H_5$, Yield: 62%; K 59.3 Ch (□) I.

MS (m/z) 380 ($M^+$), 203.

$^1$H NMR ($CDCl_3$) δ 0.85 - 1.0 (6H, m, $CH_3$), 1.1 - 1.65 (7H, m, alkyl), 1.84 (2H, m, alkyl), 2.15 (2H, m, alkyl), 2.61 (2H, t, $ArCH_2$), 4.03 (2H, t, $CH_2O$), 5.04 (2H, m, alkene), 5.84 (1H, m, alkene), 6.96, 7.08, 7.22, 8.13 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1730 (C=O), 1610, 1515 (C=C), 1260 - 1285, 1215, 1170, 1075 (C-O).

$[\alpha]_D^{25}$ ($CHCl_3$) -4.3°.

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* Data specific to 5-spacer compound. NMR and IR spectra for **7a** were representative of those for **7b**.

□ Phase transition temperature difficult to determine due to fast recrystallisation.

**7d** : n = 6, X = $C_5H_{11}$, Yield: 72%; K 50.0 N (41.2) I.

MS (m/z) 366 ($M^+$), 203.

$^1H$ NMR ($CDCl_3$) δ 0.92 (3H, t, $CH_3$), 1.34 (4H, m, alkyl), 1.6 (4H, m, alkyl), 1.84 (2H, m, alkyl), 2.15 (2H, m, alkyl), 2.61 (2H, t, $ArCH_2$), 4.03 (2H, t, $CH_2O$), 5.04 (2H, m, alkene), 5.84 (1H, m, alkene), 6.96, 7.08, 7.22, 8.13 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1730 (C=O), 1610, 1515 (C=C), 1255, 1205, 1175 (C-O), 850 (1, 4 disub).

**7e** : n = 6, X = $OCH_3$, supplied by BDH Limited; K 65.0 N (58.0) I.

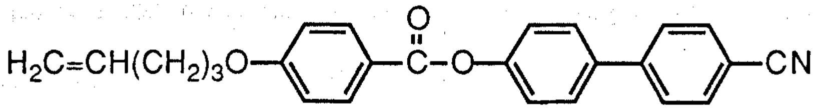
**7f** : n = 6, X = $OC_9H_{19}$, Yield: 70%; K 57.2 $S_C$ (43.0) N 76.4 I.

MS (m/z) 438 ($M^+$), 203.

$^1H$ NMR ($CDCl_3$) δ 0.88 (3H, t, $CH_3$), 1.23 - 1.64 (14H, m, alkyl), 1.81 (4H, m, alkyl), 2.14 (2H, m, alkyl), 3.95, 4.05 (2H, t, $CH_2O$), 5.04 (2H, m, alkene), 5.84 (1H, m, alkene), 6.91, 6.95, 7.08, 8.12 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 1730 (C=O), 1610, 1515 (C=C), 1255, 1205, 1175 (C-O), 850 (1, 4 disub).

*4-Cyanobiphenyl-4'-yl 4-ω-pentenyloxybenzoates (8)*



A mixture of 4-ω-pentenyloxybenzoic acid (2.06 g, 0.01 mol), 4-cyano-4'-hydroxybiphenyl (1.95 g, 0.01 mol), *N,N'*-dicyclohexylcarbodiimide (2.47 g, 0.012 mol) and 4-(*N*-pyrrolidino)pyridine (0.37 g, 2.5 x $10^{-3}$ mol) in dry dichloromethane (50 ml) was stirred overnight at room temperature with the exclusion of moisture. The substituted urea was filtered off and the product was purified by column chromatography (silica gel), eluting with a 4:1 mixture of dichloromethane:petroleum fraction [bp 40-60 °C]. Crystallisation from ethanol afforded the product as white plates.

**8** : Yield: 78%; K 108.0 N 264.5 I.

MS (m/z) 383 ($M^+$), 189, 121.

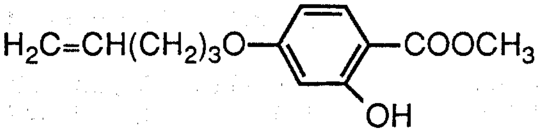
$^1H$ NMR ($CDCl_3$) δ 1.94 (2H, m, alkyl), 2.27 (2H, m, alkyl), 4.07 (2H, t, $CH_2O$), 5.04 (2H, m, alkene), 5.86 (1H, m, alkene), 7.0, 7.32 (2H, d, aromatic), 7.6 - 7.8 (6H, m, aromatic), 8.16 (2H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 2230 (C≡N), 1740 (C=O), 1605 (C=C), 1250, 1165 (C-O).

### 3.1.3 Scheme C -

### Synthesis of 4-cyanophenyl 2-alkoxy-4-ω-pentenyloxybenzoates and 4-cyanobiphenyl-4'-yl 2-alkoxy-4-ω-pentenyloxybenzoates

*Methyl 2-hydroxy-4-ω-pentenyloxybenzoate (9)*



Methyl 2, 4-dihydroxybenzoate (8.40 g, 0.05 mol), 5-bromopent-1-ene (7.50 g, 0.05 mol) and anhydrous potassium carbonate (34.50 g, 0.25 mol) in dry butanone (200 ml) were stirred and heated under reflux, with the exclusion of moisture, until completion of the reaction (TLC). The potassium carbonate was filtered off and the crude product, isolated from the filtrate as a colourless oil, was purified by column chromatography (silica gel), eluting with dichloromethane.

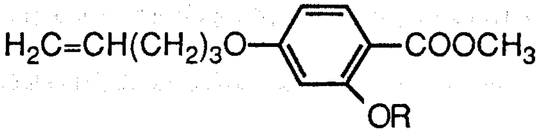
9 : Yield: 76%.

MS (m/z) 236 ($M^+$), 168, 136.

$^1$H NMR ($CDCl_3$) δ 1.86, 2.21 (2H, m, alkyl), 3.88 (3H, s, $CH_3O$), 3.97 (2H, t, $CH_2O$), 5.04 (2H, m, alkene), 5.83 (1H, m, alkene), 6.41 (2H, m, aromatic), 7.71 (1H, d, aromatic), 10.95 (1H, s, OH).

IR (Film) νmax $cm^{-1}$ 3100 - 3220 (O-H), 1680 (C=O), 1620 (C=C), 1260 (C-O).

*Methyl 2-alkoxy-4-ω-pentenyloxybenzoates (10)*



Methyl 2-hydroxy-4-ω-pentenyloxybenzoate (2.36 g, 0.01 mol), the appropriate alkyl bromide (0.012 mol) and anhydrous potassium carbonate (6.90 g, 0.05 mol) in dry butanone (100 ml) were stirred, with the exclusion of moisture and under reflux conditions, until completion of reaction (TLC). The potassium carbonate was filtered off and the solvent was distilled off under reduced pressure to leave a yellow oil (single spot -- TLC), which was used in the next step without further purification. Yields in excess of 95% were normally obtained.

**10a** : R = $C_2H_5$

MS (m/z) 264 ($M^+$), 196, 136.

$^1$H NMR ($CDCl_3$) δ 1.48 (3H, t, $CH_3$), 1.9 (2H, m, alkyl), 2.23 (2H, m, alkyl), 3.85 (3H, s, $CH_3O$), 3.98 (2H, t, $CH_2O$), 4.10 (2H, q, $CH_2O$), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.43 (2H, m, aromatic), 7.83 (1H, d, aromatic).

IR (Film) vmax $cm^{-1}$ 1730 (C=O), 1610 (C=C), 1250 - 1280, 1200 (C-O).

**10b** : R = $C_4H_9$

MS (m/z) 292 ($M^+$), 168, 136.

$^1$H NMR ($CDCl_3$) δ 0.97 (3H, t, $CH_3$), 1.55 (2H, m, alkyl), 1.86 (4H, m, alkyl), 2.24 (2H, m, alkyl), 3.82 (3H, s, $CH_3O$), 3.9 (4H, m, $CH_2O$), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.43 (2H, m, aromatic), 7.83 (1H, d, aromatic).

**10c** : R = $C_8H_{17}$

MS (m/z) 348 ($M^+$), 168, 136.

$^1$H NMR ($CDCl_3$) δ 0.9 (3H, t, $CH_3$), 1.15 - 1.55 (10H, m, alkyl), 1.85 (4H, m, alkyl), 2.23 (2H, m, alkyl), 3.4 (2H, t, $CH_2O$), 3.85 (3H, s, $CH_3O$), 3.98 (2H, t, $CH_2O$), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.43 (2H, m, aromatic), 7.83 (1H, d, aromatic).

**10d** : R = $CH_3$

MS (m/z) 250 ($M^+$), 182, 136.

$^1$H NMR ($CDCl_3$) δ 1.9 (2H, m, alkyl), 2.24 (2H, m, alkyl), 3.84 (3H, s, $CH_3O$), 3.88 (3H, s, $CH_3O$), 3.98 (2H, t, $CH_2O$), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.43 (2H, m, aromatic), 7.83 (1H, d, aromatic).

**10e** : R = $C_3H_7$

MS (m/z) 278 ($M^+$), 168, 136.

$^1$H NMR ($CDCl_3$) δ 1.06 (3H, t, $CH_3$), 1.9 (4H, m, alkyl), 2.24 (2H, m, alkyl), 3.82 (3H, s, $CH_3O$), 3.9 (4H, m, $CH_2O$), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.43 (2H, m, aromatic), 7.83 (1H, d, aromatic).

---

IR spectrum for **10a** was representative of those for **10b - g**.

**10f** : R = $C_6H_{13}$

MS (m/z) 320 ($M^+$), 168, 136.

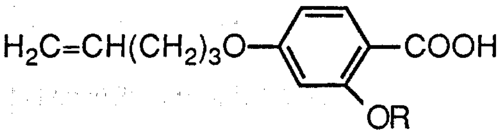
$^1H$ NMR ($CDCl_3$) δ 0.9 (3H, t, $CH_3$), 1.2 - 1.55 (6H, m, alkyl), 1.88 (4H, m, alkyl), 2.23 (2H, m, alkyl), 3.82 (3H, s, $CH_3O$), 3.9 (4H, m, $CH_2O$), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.43 (2H, m, aromatic), 7.83 (1H, d, aromatic).

**10g** : R = $CH_2CH(CH_3)C_2H_5$

MS (m/z) 306 ($M^+$), 168, 136.

$^1H$ NMR ($CDCl_3$) δ 0.95 (3H, t, $CH_3$), 1.06 (3H, d, $CH_3$), 1.33 (1H, m, alkyl), 1.88 (4H, m, alkyl), 2.24 (2H, m, alkyl), 3.82 (3H, s, $CH_3O$), 3.9 (4H, m, $CH_2O$), 5.05 (2H, m, alkene), 5.85 (1H, m, alkene), 6.43 (2H, m, aromatic), 7.83 (1H, d, aromatic).

### *2-Alkoxy-4-ω-pentenyloxybenzoic acids (11)*



Sodium hydroxide pellets (2.0 g, 0.05 mol) were dissolved in a heated mixture of methanol (60 ml) and water (10 ml). The appropriate methyl 2-alkoxy-4-ω-pentenyloxybenzoate (0.01 mol) was added and the mixture heated under reflux for 2 hours. The methanol was removed under reduced pressure and water (100 ml) was added to dissolve the white residue. Acidification (Congo Red) with concentrated hydrochloric acid gave a white precipitate which was extracted into chloroform (2 x 100 ml). The extracts were washed with saturated brine (2 x 100 ml) and dried ($MgSO_4$). The chloroform was removed under reduced pressure and the product crystallised from ethanol:water to afford the acids as white microcrystals.

**11a** : R = $C_2H_5$, Yield: 88%; m.p. 71.5 - 72.5 °C.

MS (m/z) 250 ($M^+$), 182, 136.

$^1H$ NMR ($CDCl_3$) δ 1.55 (3H, t, $CH_3$), 1.91 (2H, m, alkyl), 2.23 (2H, m, alkyl), 4.02 (2H, t, $CH_2O$), 4.26 (2H, q, $CH_2O$), 5.06 (2H, m, alkene), 5.83 (1H, m, alkene), 6.55 (2H, m, aromatic), 8.1 (1H, d, aromatic), 10.75 (1H, s, COOH).

IR (KCl) νmax $cm^{-1}$ 2550 - 3100 (O-H), 1700 (C=O), 1610 (C=C), 1250 - 1280, 1205 (C-O), 955 (O-H).

**11b** : R = $C_4H_9$, Yield: 47%; m.p. 130.0 - 131.0 °C.

MS (m/z) 278 ($M^+$), 154, 136.

$^1$H NMR ($CDCl_3$) δ 0.96 (3H, t, $CH_3$), 1.55 (2H, m, alkyl), 1.84 (4H, m, alkyl), 2.24 (2H, m, alkyl), 4.02 (2H, t, $CH_2O$), 4.2 (2H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.83 (1H, m, alkene), 6.55 (2H, m, aromatic), 8.1 (1H, d, aromatic).

**11c** : R = $C_8H_{17}$, Yield: 70%; m.p. 62.5 - 63.5 °C.

MS (m/z) 334 ($M^+$), 154, 136.

$^1$H NMR ($CDCl_3$) δ 0.88 (3H, t, $CH_3$), 1.2 - 1.6 (10H, m, alkyl), 1.9 (4H, m, alkyl), 2.25 (2H, m, alkyl), 4.02 (2H, t, $CH_2O$), 4.2 (2H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.83 (1H, m, alkene), 6.55 (2H, m, aromatic), 8.1 (1H, d, aromatic), 10.75 (1H, s, COOH).

**11d** : R = $CH_3$, Yield: 68%; m.p. 71.0 - 72.0 °C.

MS (m/z) 236 ($M^+$), 168, 136.

$^1$H NMR ($CDCl_3$) δ 1.91, 2.24 (2H, m, alkyl), 4.04 (5H, t, $CH_2O$, $CH_3O$), 5.04 (2H, m, alkene), 5.84 (1H, m, alkene), 6.52 (1H, s, aromatic), 6.64, 8.12 (1H, d, aromatic), 10.5 (1H, s, COOH).

**11e** : R = $C_3H_7$, Yield: 75%; m.p. 94.5 - 95.5 °C.

MS (m/z) 264 ($M^+$), 154, 136.

$^1$H NMR ($CDCl_3$) δ 1.06 (3H, t, $CH_3$), 1.9 (4H, m, alkyl), 2.24 (2H, m, alkyl), 4.03 (2H, t, $CH_2O$), 4.18 (2H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.83 (1H, m, alkene), 6.55 (2H, m, aromatic), 8.1 (1H, d, aromatic), 10.75 (1H, s, COOH).

**11f** : R = $C_6H_{13}$, Yield: 57%; m.p. 61.2 - 62.2 °C.

MS (m/z) 306 ($M^+$), 154, 136.

$^1$H NMR ($CDCl_3$) δ 0.88 (3H, t, $CH_3$), 1.3 - 1.6 (6H, m, alkyl), 1.9 (4H, m, alkyl), 2.25 (2H, m, alkyl), 4.02 (2H, t, $CH_2O$), 4.2 (2H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.83 (1H, m, alkene), 6.55 (2H, m, aromatic), 8.1 (1H, d, aromatic).

**11g** : R = $CH_2CH(CH_3)C_2H_5$, Yield: 63%; m.p. 60.5 - 61.5 °C.

MS (m/z) 292 ($M^+$), 154, 136.

$^1$H NMR ($CDCl_3$) δ 0.95 (3H, t, $CH_3$), 1.06 (3H, d, $CH_3$), 1.33 (1H, m, alkyl), 1.88 (4H, m, alkyl), 2.24 (2H, m, alkyl), 4.03 (2H, t, $CH_2O$), 4.24 (2H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.83 (1H, m, alkene), 6.55 (2H, m, aromatic), 8.1 (1H, d, aromatic).

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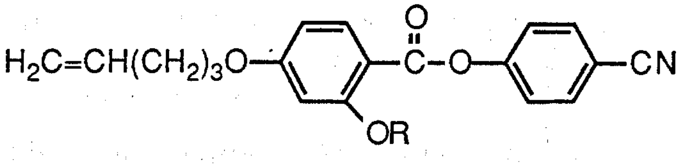
IR spectrum for **11a** was representative of those for **11b - g**.

*4-Cyanophenyl 2-alkoxy-4-ω-pentenyloxybenzoates (**12**)*



A mixture of the appropriate 2-alkoxy-4-ω-pentenyloxybenzoic acid (1.0 g, 0.004 mol), 4-cyanophenol (0.48 g, 0.004 mol), *N,N'*-dicyclohexylcarbodiimide (1.0 g, 4.8 x $10^{-3}$ mol) and 4-(*N*-pyrrolidino)pyridine (0.15 g, 1 x $10^{-4}$ mol) in dry dichloromethane (30 ml) was stirred overnight at room temperature with the exclusion of moisture. The substituted urea was filtered off and the crude product obtained from the filtrate was purified by flash chromatography (silica gel), eluting with dichloromethane. Crystallisation from petroleum fraction [bp 40-60 °C] afforded the product as white crystals.

**12a** : R = $C_2H_5$, Yield: 41%; m.p. 54.0 - 55.0 °C.

MS (m/z) 351 ($M^+$), 233, 137.

$^1H$ NMR ($CDCl_3$) δ 1.49 (3H, t, $CH_3$), 1.93 (2H, m, alkyl), 2.25 (2H, m, alkyl), 3.95 - 4.15 (4H, m, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.34, 7.71 (2H, d, aromatic), 8.03 (1H, d, aromatic).

IR (KCl) vmax $cm^{-1}$ 2230 (C≡N), 1740 (C=O), 1600 (C=C), 1200 (C-O).

**12b** : R = $C_4H_9$, Yield: 46%; m.p. 68.7 - 69.7 °C.

MS (m/z) 379 ($M^+$), 261, 137.

$^1H$ NMR ($CDCl_3$) δ 0.95 (3H, t, $CH_3$), 1.54 (2H, m, alkyl), 1.86 (4H, m, alkyl), 2.26 (2H, m, alkyl), 4.05 (4H, m, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.34, 7.71 (2H, d, aromatic), 8.03 (1H, d, aromatic).

**12c** : R = $C_8H_{17}$, Yield: 41%; m.p. 41.4 - 42.4 °C.

MS (m/z) 435 ($M^+$), 317, 137.

$^1H$ NMR ($CDCl_3$) δ 0.86 (3H, t, $CH_3$), 1.15 - 1.6 (10H, m, alkyl), 1.86 (4H, m, alkyl), 2.26 (2H, m, alkyl), 4.04 (4H, m, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.34, 7.71 (2H, d, aromatic), 8.03 (1H, d, aromatic).

---

IR spectrum for **12a** was representative of those for **12b** - **e**.

**12d** : R = $CH_3$, Yield: 49%; m.p. 89.8 - 90.8 °C.

MS (m/z) 337 ($M^+$), 219, 137.

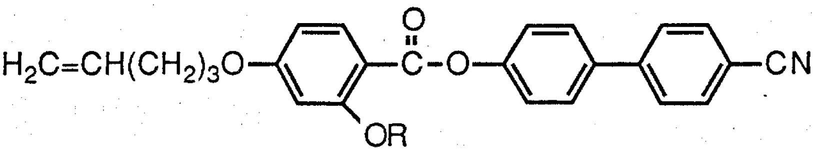
$^1H$ NMR ($CDCl_3$) δ 1.93 (2H, m, alkyl), 2.26 (2H, m, alkyl), 3.94 (3H, s, $CH_3O$), 4.06 (2H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.34, 7.71 (2H, d, aromatic), 8.03 (1H, d, aromatic).

**12e** : R = $C_3H_7$, Yield: 70%; m.p. 72.7 - 73.7 °C.

MS (m/z) 365 ($M^+$), 247, 137.

$^1H$ NMR ($CDCl_3$) δ 1.06 (3H, t, $CH_3$), 1.91 (4H, m, alkyl), 2.26 (2H, m, alkyl), 4.03 (4H, m, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.34, 7.71 (2H, d, aromatic), 8.03 (1H, d, aromatic).

*4-Cyanobiphenyl-4'-yl 2-alkoxy-4-ω-pentenyloxybenzoates (13)*



A mixture of the appropriate 2-alkoxy-4-ω-pentenyloxybenzoic acid (1.0 g, 0.004 mol), 4-cyano-4'-hydroxybiphenyl (0.78 g, 0.004 mol), *N,N'*-dicyclohexylcarbodiimide (1.0 g, 4.8 x $10^{-3}$ mol) and 4-(*N*-pyrrolidino)pyridine (0.15 g, 1 x $10^{-4}$ mol) in dry dichloromethane (30 ml) was stirred overnight at room temperature with the exclusion of moisture. The substituted urea was filtered off and the crude product obtained from the filtrate was purified by flash chromatography (silica gel), eluting with dichloromethane. Crystallisation from petroleum fraction [bp 40-60 °C]:toluene afforded the product as white crystals.

**13a** : R = $C_2H_5$, Yield: 47%; K 100.6 N 107.6 I.

MS (m/z) 427 ($M^+$), 233, 137.

$^1H$ NMR ($CDCl_3$) δ 1.49 (3H, t, $CH_3$), 1.93 (2H, m, alkyl), 2.27 (2H, m, alkyl), 4.06 (2H, t, $CH_2O$), 4.14 (2H, q, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.32 (2H, d, aromatic), 7.6 - 7.75 (6H, m, aromatic), 8.06 (1H, d, aromatic).

IR (KCl) νmax $cm^{-1}$ 2230 (C≡N), 1735 (C=O), 1610 (C=C), 1205, 1170, 1135 (C-O).

**13b** : R = $C_4H_9$, Yield: 31%; K 103.7 N (65.0) I.

MS (m/z) 455 ($M^+$), 261, 137.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.96 (3H, t, $CH_3$), 1.54 (2H, m, alkyl), 1.88 (4H, m, alkyl), 2.27 (2H, m, alkyl), 4.06 (4H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.32 (2H, d, aromatic), 7.6 - 7.75 (6H, m, aromatic), 8.06 (1H, d, aromatic).

**13c** : R = $C_8H_{17}$, Yield: 80%; K 58.5 N (38.8) I.

MS (m/z) 511 ($M^+$), 317, 137.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.88 (3H, t, $CH_3$), 1.17 - 1.6 (10H, m, alkyl), 1.88 (4H, m, alkyl), 2.27 (2H, m, alkyl), 4.06 (4H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.32 (2H, d, aromatic), 7.6 - 7.75 (6H, m, aromatic), 8.06 (1H, d, aromatic).

**13f** : R = $C_6H_{13}$, Yield: 75%; K 83.4 N (43.8) I.

MS (m/z) 483 ($M^+$), 289, 137.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.88 (3H, t, $CH_3$), 1.32 (4H, m, alkyl), 1.52 (2H, m, alkyl), 1.88 (4H, m, alkyl), 2.26 (2H, m, alkyl), 4.06 (4H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.32 (2H, d, aromatic), 7.6 - 7.75 (6H, m, aromatic), 8.06 (1H, d, aromatic).

**13g** : R = $CH_2CH(CH_3)C_2H_5$, Yield: 45%; K 81.2 Ch (40.5) I.

MS (m/z) 469 ($M^+$), 275, 137.

$^1H$ NMR ($CDCl_3$) $\delta$ 0.91 (3H, t, $CH_3$), 1.06 (3H, d, $CH_3$), 1.32 (1H, m, alkyl), 1.91 (4H, m, alkyl), 2.26 (2H, m, alkyl), 4.06 (4H, t, $CH_2O$), 5.06 (2H, m, alkene), 5.86 (1H, m, alkene), 6.54, 7.32 (2H, d, aromatic), 7.6 - 7.75 (6H, m, aromatic), 8.06 (1H, d, aromatic).

$[\alpha]_D^{25}$ ($CHCl_3$) +6.6°.

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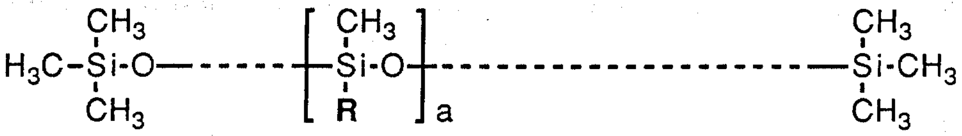
IR spectrum for **13a** was representative of those for **13b, c, f** and **g**.

# 3.2 SIDE CHAIN POLYSILOXANES

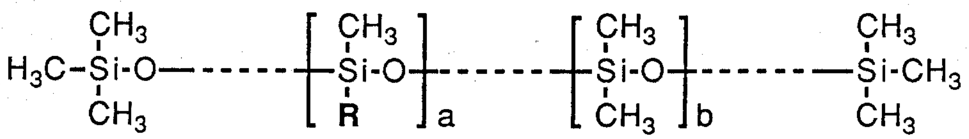
## 3.2.1 Side Chain Homo- and Co- polymers (W)



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O-\cdots-\left[\overset{CH_3}{\underset{R}{Si}}-O\right]_a-\cdots-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

Poly(hydrogenmethylsiloxane) (0.18 g, 0.003 mol/Si-H) and the appropriate alkene or mixture of alkenes (10 mol-% excess) were dissolved in dry toluene (20 ml) and the solution degassed with $N_2$. The catalyst -- hexachloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$, 0.02 g) in propan-2-ol (5 ml) or an accurately measured volume of a solution of known concentration of platinum divinyltetramethyldisiloxane complex (PVMS) in xylene -- was added to the reaction mixture such that a Pt:alkene ratio in the range 1:$10^3$ - $10^6$ mol was obtained. The solution was stirred and heated under reflux, with eventual further addition(s) of catalyst if necessary, until the Si-H absorption in the infra-red spectrum (2160 $cm^{-1}$) had been reduced to a residual level -- normally after 24 hours. The solvent was removed under reduced pressure to leave the crude polymer, which was dissolved in dry dichloromethane and purified by repeated precipitations with dry methanol and centrifugations until free from any detectable (TLC) concentration of side chain precursor. The polymer solution in dichloromethane was then filtered using a PTFE membrane filter (0.5 μm pore size), and the solvent removed under vacuum.

### 3.2.2 Backbone Copolymer Side Chain Homo- and Co- polymers (P)



$$H_3C-\overset{CH_3}{\underset{CH_3}{Si}}-O\text{------}\left[\overset{CH_3}{\underset{R}{Si}}-O\right]_a\text{------}\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_b\text{------}\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$$

The same synthetic procedure as that described in Section 3.2.1 for the polymers (W) was used, except that the prepolymer backbone employed was a poly(hydrogenmethyldimethylsiloxane) copolymer.

The IR spectra of all the polymers (**W** and **P**) were entirely consistent with those of the side chain precursors used for attachment to the backbones in the various hydrosilylation reactions; absorptions due to the terminal -CH=$CH_2$ group were of course absent.

The $^1$H NMR ($CDCl_3$) spectra for all the polymers (**W** and **P**) were virtually identical to those of the side chain precursors involved, with the addition of signals for the silyl protons at

$\delta$ = -0.15 (3H, s, Si-$CH_3$) and 0.35 (2H, t, Si-$CH_2$),

and the loss of signals for alkenic protons at

$\delta$ = 5.0 and 5.84.

# four

# *results and discussion*

## 4.1 SIDE CHAIN PRECURSORS

The phase transition temperatures and melting points of the side chain precursors used in the synthesis of laterally, terminally and mixed laterally/terminally attached side chain liquid crystal polysiloxanes are reported in Tables 4.1 - 4.5. Many of these low molar mass precursors proved to be interesting liquid crystal materials in their own right, and their virtues are discussed alongside their polymeric analogues under the relevant sections in this chapter.

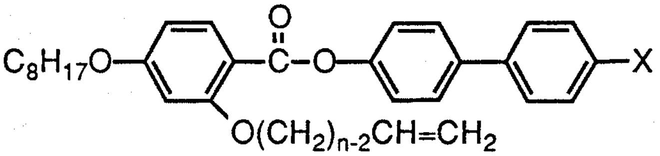
The thermal data for the SCLCP derived using these side chain precursors have been tabulated accordingly. These polymers have been allocated a sequential number for each unique system, prefixed by either W, P or Y. The letters represent the type of polymer backbone used in the synthesis of the SCLCP:

W -- Poly(hydrogenmethylsiloxane) backbone, supplied by Wacker Chemie.
P -- Poly(hydrogenmethyldimethylsiloxane) backbone, supplied by Petrarch.
Y -- Poly(hydrogenmethylsiloxane) backbone, fractionated by the York Polymer Group into sharp linear fractions from samples supplied by Dow Corning.

In addition, the acronym given to each of the side chain precursors synthesised appears alongside the results for the appropriate polymer preparation, and Tables 4.1 - 4.5 should be used as a guide to identifying the nature and composition of the liquid crystal polymer to which reference is made.

*Table 4.1*

*Key to the mesogenic side chain precursors used in the preparation of laterally attached and mixed laterally/terminally attached SCLCP of the octyloxy series and their transition temperatures (°C)*



| Cmpd No | n | X | K - N, I | N - I |
|---|---|---|---|---|
| **5a** | 5 | CN | 67.5 | (66.4) |
| **5b** | 6 | CN | 74.5 | (58.2) |
| **5c** | 5 | $C_5H_{11}$ | 44.5 | 50.2 |
| **5d** | 6 | $C_5H_{11}$ | 42.2 | 45.2 |
| **5e** | 6 | $OCH_3$ | 102.2 | (¤) |
| **5f** | 6 | $OC_2H_5$ | 98.0 | (77.5) |
| **5g** | 6 | $OC_3H_7$ | 89.2 | (51.4) |
| **5h** | 6 | $OC_4H_9$ | 80.8 | (74.0) |
| **5i** | 6 | $OC_5H_{11}$ | 75.0 | (65.5) |
| **5j** | 6 | $OC_6H_{13}$ | 63.5 | 71.6 |
| **5k** | 6 | $OC_7H_{15}$ | 57.0 | 66.5 |
| **5l** | 6 | $OC_8H_{17}$ | 50.3 | 68.9 |
| **5m** | 6 | $OC_9H_{19}$ | 46.0 | 67.6 |
| **5n** | 6 | $OC_{10}H_{21}$ | 55.0 | 68.9 |
| **5o** | 5 | $OCH_2CH(CH_3)C_2H_5$ | 67.0 | (42.8)* |
| **5p** | 5 | $OCH(CH_3)C_6H_{13}$ | 36.8 | (5.7)* |
| **5q** | 5 | $OCH(CH_3)COOC_2H_5$ | 52.0 | (-5.0)* |

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¤ Monotropic phase transition temperature difficult to determine due to fast recrystallisation.

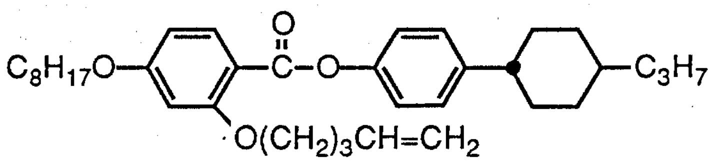
* Chiral nematic-isotropic transition.

*Table 4.1 (continued)*

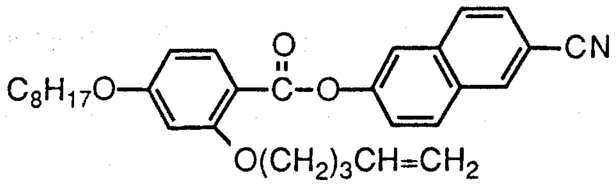
| | | | | |
|---|---|---|---|---|
| **5r** | 5 | $COOCH_3$ | 90.6 | (¤) |
| **5s** | 5 | $CH_2COOCH_3$ | 71.7 | (19.8) |
| **5t** | 5 | $(CH_2)_2COOCH_3$ | 56.0 | (29.8) |
| **5u** | 5 | $CH{=}CHCOOCH_3$ | 103.5 | 122.5 |
| **5v** | 5 | $CH(CH_3)CH_2COOCH_3$ | 54.5 | - |
| **5w** | 5 | $COOCH_2CH(CH_3)C_2H_5$ | 63.4 | (32.6)* |
| **5x** | 5 | $(CH_2)_2CH(CH_3)C_2H_5$ | 44.4 | (32.6)* |
| **5y** | 5 | $(CH_2)_3CH(CH_3)C_2H_5$ | 41.3 | (32.2)* |
| **5z** | 5 | H | 92.7 | - |
| **5aa** | 5 | F | 68.3 | (30.4) |
| **5ab** | 5 | $CF_3$ | 79.2 | (38.0) |
| **5ac** | 5 | Br | 67.7 | (49.0) |
| **5ad** | 5 | $C_3H_7$ | 57.5 | (50.3) |
| **JSH** | 11 | CN | 48.2 | (43.4) |

*Table 4.2*

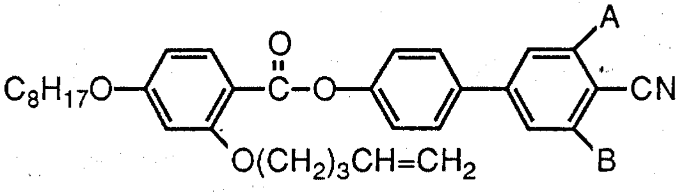
*Key to some structurally modified mesogenic side chain precursors used in the preparation of laterally attached SCLCP of the octyloxy series and their transition temperatures (°C)*



**5ae** : K 56.0 N (41.0) I.

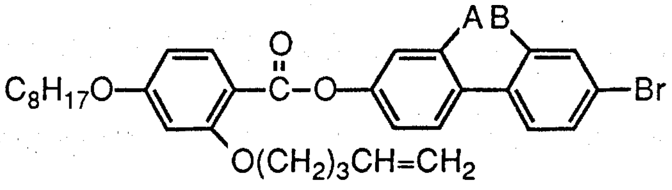


**5af** : K 61.2 N (-1.5) I.



**5ag** : A = F, B = H; K 67.5 N (39.8) I.

**5ah** : A = F, B = F; K 45.3 N (-1.7) I.

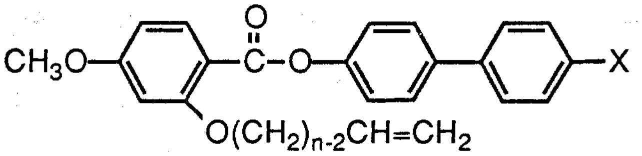


**5ai** : A = F, B = H; K 52.7 N (12.2) I.

**5aj** : A = H, B = F; K 64.0 N (20.2) I.

*Table 4.3*

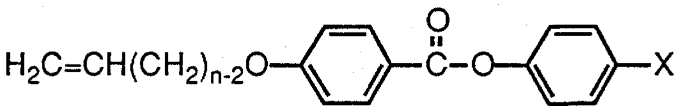
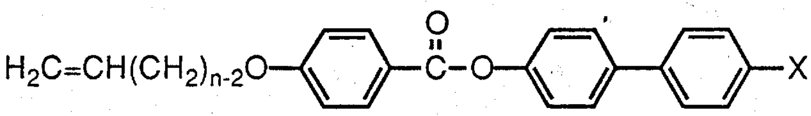
*Key to the mesogenic side chain precursors used in the preparation of laterally attached SCLCP of the methoxy series and their transition temperatures (°C)*



| Cmpd No | n | X | K - N, I | N - I |
|---|---|---|---|---|
| **5ma** | 5 | CN | 92.8 | (49.3) |
| **5mb** | 6 | CN | 110.0 | (33.5) |

*Table 4.4*

*Key to the mesogenic side chain precursors used in the preparation of terminally attached and mixed laterally/terminally attached SCLCP and their transition temperatures (°C)*

| Cmpd No | n | X | K - $S_C$, N, I | $S_C$ - N | N - I |
|---|---|---|---|---|---|
|  | | | | | |
| **7a** | 5 | CN | 77.0 | - | 77.8 |
| **7b** | 6 | CN | 63.0 | - | (62.8) |
| **7c** | 6 | $(CH_2)_2CH(CH_3)C_2H_5$ | 59.3 | - | (¤) |
| **7d** | 6 | $C_5H_{11}$ | 50.0 | - | (41.2) |
| **7e** | 6 | $OCH_3$ | 67.2 | - | (59.0) |
| **7f** | 6 | $OC_9H_{19}$ | 57.2 | (43.0) | 76.4 |
|  | | | | | |
| **8** | 5 | CN | 108.0 | - | 264.5 |

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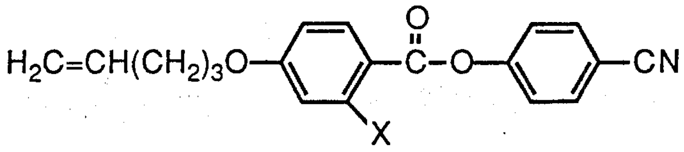
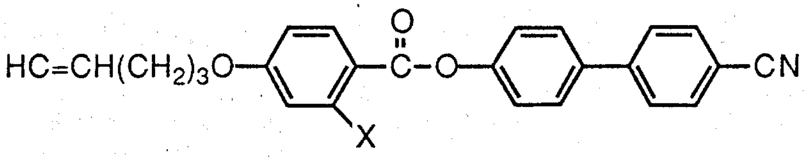
¤ Monotropic phase transition temperature difficult to determine due to fast recrystallisation.

*Table 4.5*

*Key to the mesogenic side chain precursors used in the preparation of terminally attached SCLCP and their transition temperatures (°C)*



| Cmpd No | X | K - N, I | N - I |
|---|---|---|---|
| **7a** | H | 77.0 | 77.8 |
| **12d** | $OCH_3$ | 89.8 | - |
| **12a** | $OC_2H_5$ | 54.0 | - |
| **12e** | $OC_3H_7$ | 72.7 | - |
| **12b** | $OC_4H_9$ | 68.7 | - |
| **12c** | $OC_8H_{17}$ | 41.4 | - |



| | | | |
|---|---|---|---|
| **8** | H | 108.0 | 264.5 |
| **13a** | $OC_2H_5$ | 100.6 | 107.6 |
| **13b** | $OC_4H_9$ | 103.7 | (65.0) |
| **13f** | $OC_6H_{13}$ | 83.4 | (43.8) |
| **13c** | $OC_8H_{17}$ | 58.5 | (38.8) |
| **13g** | $OCH_2CH(CH_3)C_2H_5$ | 81.2 | (40.5)* |

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* Chiral nematic-isotropic transition.

## 4.2 POLYMERS WITH LARGE POSITIVE DIELECTRIC ANISOTROPIES

In order that the commercial potential of laterally attached SCLCP might be promoted, it was preferable that polysiloxanes having large positive dielectric anisotropies be synthesised. The terminal cyano-substituent was selected because of interest in the dielectric properties that would be conferred on the polymers, possibly making them suitable for speciality applications [1, 2]. The use of these terminally cyano-substituted mesogenic side chains had caused synthetic problems in earlier work [3], but these difficulties were later overcome by Gemmell *et al.* [4]. However, all such reports referred to the terminal attachment of the mesogenic groups, whereas the object of this work was the production of polysiloxanes with laterally attached cyano-substituted mesogenic groups.

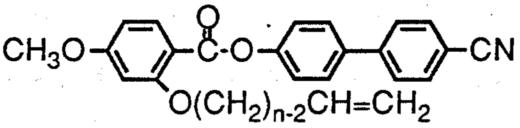
### 4.2.1 Side Chain Homopolymers

The first series of polymers synthesised had mesogenic groups with methoxy groups on the left terminus of the side chain. It is noted that although the respective side chain precursors are nematic (Table 4.3), the derived polymers show no mesophases and are in fact crystalline polymers, with crystal-isotropic liquid (K - I) transitions (Table 4.6). Optical microscopy failed to show any birefringence in the supercooled isotropic phase. This was an early indication that the behaviour of laterally attached side chain polymers are not always strictly analogous to those that have terminally attached side chains. The so called 'polymer effect', observed with most polymers and especially for the terminally attached side chain variety, whereby enhancements in mesomorphism are observed on passing from a monomeric to a polymeric system [5], is clearly not applicable in these examples.

*Table 4.6*

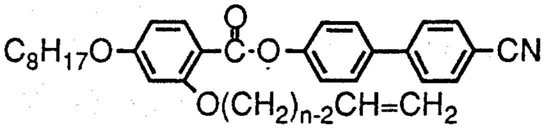
*Phase transition temperatures and enthalpies of clearing for laterally attached side chain polysiloxane homopolymers of the methoxy and octyloxy series, showing the effect of catalyst type*

*Methoxy series*



| | | TYPE | K - I t/°C | ΔH cal/g |
|---|---|---|---|---|
| W1 | **5ma** | H | 60.0 | 1.66 |
| W2 | **5ma** | P | 60.2 | 1.55 |
| W3 | **5mb** | H | 52.0 | 1.79 |
| W4 | **5mb** | P | 53.6 | 1.60 |

*Octyloxy series*



| | | TYPE | Tg t/°C | | N - I t/°C | | ΔH cal/g |
|---|---|---|---|---|---|---|---|
| | | | ONSET | MID-PT | ONSET | MAX | |
| W5 | **5a** | H | 14.1 | 15.7 | 64.2 | 68.6 | 0.17 |
| W6 | **5a** | P | 28.7 | 29.4 | 84.6 | 89.8 | 0.24 |
| W7 | **5b** | H | 9.7 | 11.8 | 63.2 | 67.7 | 0.17 |
| W8 | **5b** | H/C | 11.2 | 12.5 | 73.4 | 76.8 | 0.20 |
| W9 | **5b** | P | 22.0 | 25.1 | 77.5 | 82.1 | 0.23 |

H Hexachloroplatinic acid ($H_2PtCl_6$).

H/C Hexachloroplatinic acid, followed by purification of polymer by column chromatography.

P Platinum divinyltetramethyldisiloxane complex (PVMS).

The clearing temperatures for the octyloxy polymers with terminal cyano-substituents (Table 4.6), however, are higher than those for the side chain precursors (Table 4.1). Although this now agrees with literature reports concerning side chain precursors and the derived polymers with either terminally [4, 5] or laterally attached [6, 7] mesogenic groups, this trend is reversed when the cyano-group in the laterally attached systems now under study is replaced by an alkyl or alkoxy group. More will be said of this feature later, but it is thought that this odd result, i.e., increased transition temperatures in the polymers produced from these novel side chain systems, could simply be a consequence of different extents/types of pairwise correlations involving the terminal polar group.

Long spacers and long terminal alkyl groups and terminal polar groups in the mesogenic moieties encourage the formation of smectic phases in terminally attached SCLCP [5]. However, the two laterally attached side chain LCP shown in Table 4.6 (derived from **5a** and **5b**) both exhibit nematic phases, despite the terminal $C_8O$ and CN groups and the use of 6 and 7 atom spacers. The clearing enthalpies obtained from DSC all lie in the range 0.1 - 0.3 cal/g, values which are typical of those associated with isotropisation of nematic phases. The phase assignments were further confirmed by optical microscopy. Orthoscopic observation of the mesophases of the polymers revealed mainly birefringent homogeneous regions and/or mottled, sanded regions (probably fine schlieren texture with a high density of defects), characteristic of the nematic phase (Plates 5 and 6). The textures were normally recognisable after annealing for just a few minutes and the phases were quite fluid.

As might be anticipated for a polymer which has rotation around the molecular long axes of its side chains prevented by the lateral connection to the polymer backbone [6], optical biaxiality is observed. Macroscopic homeotropic alignment of the sample was achieved by application of an a.c. voltage (100 V, 50 Hz, one hour), across a cell of thickness 25 μm filled with the terminally cyano-substituted SCLCP (W6). Conoscopic observations with convergent polarised light, obtained using a Bertrand lens, revealed interference patterns characteristic of the optically biaxial behaviour of the nematic phase.

**Plate 5**

*Typical 'sandy' texture of the nematic phase of a laterally attached side chain liquid crystal polysiloxane, crossed polarisers (x 100).*

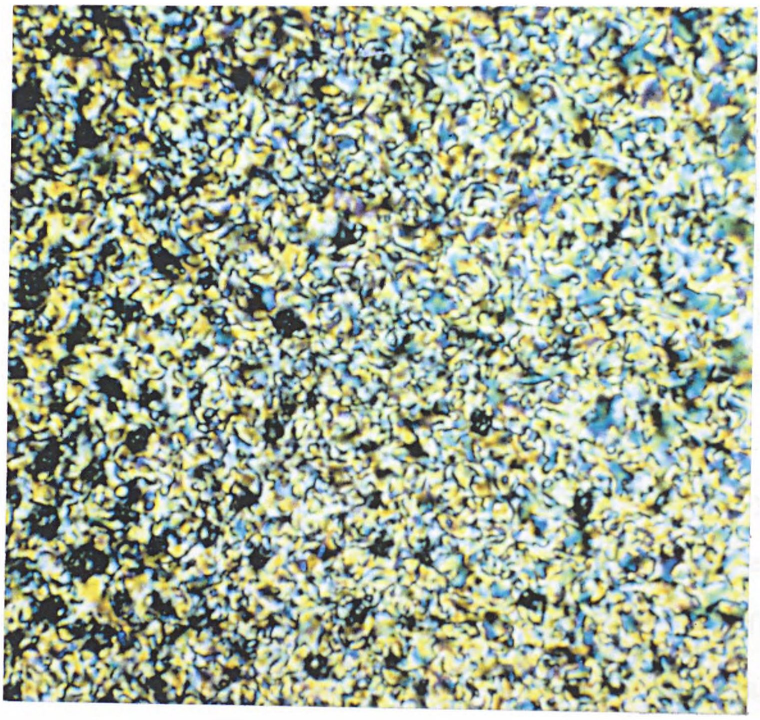


**Plate 6**

*Same preparation photographed after annealing for one hour at 5 °C below its clearing temperature. Notice that the characteristic nematic schlieren texture is more clearly defined, crossed polarisers (x 100).*

The combination of a laterally attached, terminally cyano-substituted side chain with the flexible polysiloxane backbone -- known to encourage low glass transition and clearing temperatures [8] -- has thus given rise to novel side chain liquid crystal polymers with biaxial nematic phases just above ambient temperature.

It has been reported that anomalous $\alpha$-addition of hydrogen at the double bond can occur in hydrosilylations catalysed by hexachloroplatinic acid [9]; the cases quoted involved terminally attached side chains and allyl carbonate spacer groups. This was not found to be the case in earlier studies involving hexachloroplatinic acid and terminally attached mesogenic groups [10], but it was soon apparent in the present work with laterally attached mesogenic groups, that $\alpha$-addition of hydrogen does occur, and with $\omega$-alkenyloxy spacers longer than allyl carbonate. This was confirmed by $^1H$ NMR spectroscopy ($\delta$ (p.p.m.) 1.1), which showed that the unwanted $\alpha$-form could contribute as much as 30% to the final polymer products obtained by the lateral attachment of the cyano-substituted side chains (Figure 2.3).

The anomalous addition observed with hexachloroplatinic acid did not appear to take place with the Petrarch catalyst, platinum divinyltetramethyldisiloxane complex (PVMS). The repercussions of this change in catalyst and the associated prevention of the formation of anomalous addition products are readily seen by comparing the transition temperatures recorded in Table 4.6 for the two pairs of terminally cyano-substituted polysiloxanes (W5 and W6; W7 and W9) prepared using both catalysts.

The transition temperatures for the methoxy series are found to be unaffected by the $\alpha$-addition products formed when using hexachloroplatinic acid. However, these polymers are not mesomorphic, having neither Tg nor clearing temperatures. These polymers exhibit only $T_{K\text{-}I}$ values which are probably less sensitive to structural changes. The terminal cyano-substituted polymers of the octyloxy series made with PVMS, on the other hand, have significantly higher phase transition temperatures than their equivalents synthesised using hexachloroplatinic acid. This is attributed to the prevention of anomalous addition products using PVMS; the presence of a 30% population of the anomalous α-form -- which causes branching of the spacer and an associated steric effect -- is probably responsible for the observed temperature suppression of the Tg and $T_{N-I}$ values. These transitions are therefore more sensitive to structural factors than the crystal-isotropic transitions of the polymers with terminal methoxy groups.

In addition, the terminal cyano-substituted polymer of the octyloxy series with a six carbon spacer which was prepared using hexachloroplatinic acid was further purified by silica gel column chromatography. This was performed to see if the colour of the polymer, caused by the high catalyst concentration, could be improved. The column was first eluted with diethyl ether, which removed low molar mass oligomers (as observed by TLC), followed by dichloromethane. The polymer collected was white, while the colouration remained visible on the column. Gel permeation chromatography of the preparation before and after column chromatography revealed a small reduction in the polydispersity of the polymer from 2.5 to 2.2. The lower value in polydispersity after column purification is explained by the removal of the low molar mass oligomers mentioned above, thereby reducing the spread of polymer chains with different molecular weights. The phase transition temperatures are consequently enhanced (*cf.*, results for W8 and W7). This outcome is not unexpected, since the presence of low molar mass materials is known to adversely affect the thermal properties of polymers [11]. However, the transition temperatures for polymer W8 are still much lower than those for the analogous polymer made using PVMS (W9), and column chromatography clearly does not separate out polymer components involving anomalously added side chains. Indeed it was not anticipated that this would occur.

These observations concerning column chromatography raised the question of the feasibility of using this technique for all future preparations, i.e., of using column chromatography both to decolourise the polymer and 'transform' the product into a less polydisperse system than the original preformed backbone. Although it could be argued that a cleaner polymer with sharper transition temperatures would be obtained, it was strongly felt that for this work, the inevitable variations in polydispersity that would arise through using column chromatography on a range of different polymers would complicate the results, i.e., the variations in the final materials would then not permit direct comparisons to be made on a structural basis, since allowances would have to be made for differences in polydispersity.

### 4.2.2 Polar Group Dilution

The large positive dielectric anisotropy which should be conferred on these polymers, by the terminal cyano-substituents of the mesogenic groups, make the materials attractive. The situation is, however, complicated by the likelihood that antiparallel pairwise correlations of molecular dipoles will occur at the molecular level. As in low molar mass systems, these will result from the overlap of adjacent cyano-substituted mesogenic units [12], and in the case of polymeric systems these can occur both intra- and intermolecularly. Such correlations would reduce the contribution of the dipole moment of the cyano-group parallel to the long axis of the mesogenic side chain and lead to a suppression of $\Delta\varepsilon$ for the system [13].

In the case of low molar mass materials consisting of terminally cyano-substituted mesogens that are required for multiplex addressed twisted nematic displays, it is important, for good performance, that such materials should have a very sharp threshold response to an applied voltage, and this is achieved by adding terminally non-polar mesogens to the mixtures so that the antiparallel pairwise correlations are diminished [14]. It was envisaged that a similar effect could be achieved in laterally attached SCLCP by the incorporation of cyano-substituted and non-cyano-substituted mesogenic groups on the same homopolymer backbone. By the creation of this statistical distribution of two mesogenic side chains along a preformed backbone, it was assumed that the non-polar groups would effectively prevent intramolecular associations of the polar end-groups, and to a lesser extent, would reduce intermolecular correlations. Although it would be naive to expect complete segregation of the polar groups, it was believed therefore that in these side chain copolymers, antiferroelectric short range ordering would at least be reduced.

The side chain homopolymers, derived from alkenes with terminal non-polar groups, were also investigated (Table 4.7). As stated in the previous section, these laterally attached homopolymers with terminal alkyl groups (W10 and W11) are found to have lower transition temperatures than those observed for the side chain precursors (average decrease for **5c** and **5d** = 5.7 °C), a view not wholly in support of current literature claims relating to other laterally attached SCLCP [6, 7]. The terminally cyano-substituted side chain precursor **5a** has of course a much higher $T_{N-I}$ value than the terminally pentyl-substituted equivalent **5c** (by 16.2 °C) and the corresponding polymers W6 and W10 differ in $T_{N-I}$ by 47.4 °C, the cyano polymer again having the higher clearing temperature. This is entirely in accordance with the long known fact that the cyano-group lies high in the order of terminal substituents promoting nematic properties relative to alkyl groups or hydrogen [15].

The phase transition temperatures of the side chain homopolymers W6 and W10 and of the copolymers W13 - 15 are given in Table 4.7 and expressed graphically in Figure 4.1. The first observation that may be drawn from the graph is that the plots for both the Tg and $T_{N-I}$ values show similar trends. For copolymer W15, with the terminally pentyl-substituted mesogenic unit in excess, $T_{N-I}$ is low, and it may be assumed that there has been extensive break up of antiparallel correlations; it is known that the degree of association in low molar mass (LMM) cyano-systems decreases quickly on dilution with non-polar mesogens. The resultant increase in the concentration of free cyano-substituted molecules has been observed to lead to depressions in N - I transition temperatures in low molar mass liquid crystal materials [16], i.e., marked negative deviations from a linear dependence of $T_{N-I}$ upon concentration of non-polar mesogens in terminally cyano-substituted hosts are known. Consequently, for the copolymers W13 and W14, with reduced concentrations of the terminally non-polar moiety, the reductions in $T_{N-I}$

*Table 4.7*

*Phase transition temperatures and enthalpies of clearing for laterally attached side chain polysiloxane homopolymers and copolymers*

*Homopolymers*

| | | X | Tg t/°C | | N - I t/°C | | ΔH cal/g |
|---|---|---|---|---|---|---|---|
| | | | ONSET | MID-PT | ONSET | MAX | |
| W4 | **5mb** | CN | - | - | - | 53.6 $^{K}$ | 1.60 |
| W6 | **5a** | CN | 28.7 | 29.4 | 84.6 | 89.8 | 0.24 |
| W9 | **5b** | CN | 22.0 | 25.1 | 77.5 | 82.1 | 0.23 |
| W10 | **5c** | $C_5H_{11}$ | -0.8 | 1.2 | 38.4 | 42.4 | 0.45 |
| W11 | **5d** | $C_5H_{11}$ | -12.4 | -8.6 | 37.0 | 41.6 | 0.45 |
| W12 | **JSH** | CN | 4.7 | 7.5 | 43.0 | 44.4 | 0.10 |

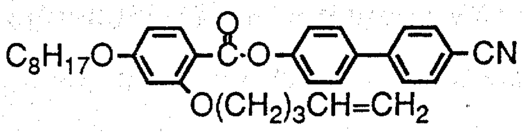
*Copolymers*

| | Alkenes mol-% | | | | Tg t/°C | | N - I t/°C | | ΔH cal/g |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | ONSET | MID-PT | ONSET | MAX | |
| W13 | **5a** | 60 | **5c** | 40 | 14.7 | 18.1 | 47.7 | 52.7 | 0.15 |
| W14 | **5a** | 50 | **5c** | 50 | 5.4 | 5.7 | 32.6 | 37.9 | 0.16 |
| W15 | **5a** | 40 | **5c** | 60 | -8.2 | -4.6 | 22.5 | 28.0 | 0.15 |
| W16 | **5a** | 60 | **JSH** | 40 | 13.1 | 15.2 | 53.2 | 56.0 | 0.10 |
| W17 | **5b** | 20 | **5mb** | 80 | 13.5 | 14.0 | - | - | - |
| W18 | **5b** | 30 | **5mb** | 70 | 30.0 | 31.0 | - | - | - |
| W19 | **5b** | 40 | **5mb** | 60 | 31.0 | 32.0 | 66.2 | 68.0 | 0.13 |
| W20 | **5b** | 50 | **5mb** | 50 | 30.0 | 33.0 | 56.6 | 59.5 | 0.06 |

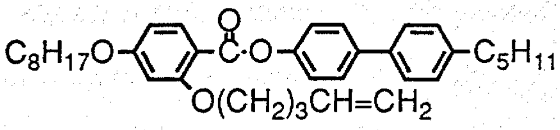
K : Crystal-isotropic transition.

*Figure 4.1*

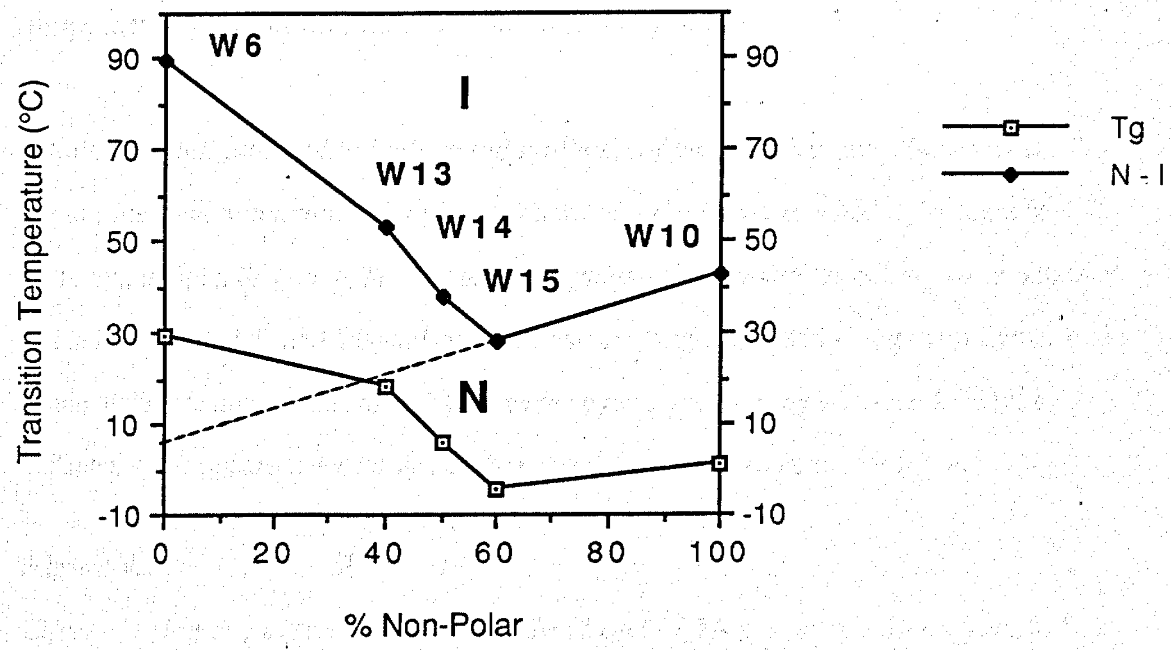
*Effect of terminal polar group (5a) dilution by terminal non-polar groups (5c) attached to the PHMS homopolymer backbone*



**5a**



**5c**



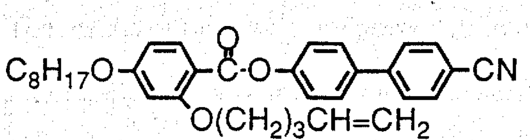
are considerably diminished. There is an approximate 25 °C increase in the nematic-isotropic transition from W15 to W13, caused by the partial re-establishment of antiparallel correlations, i.e., a higher proportion of associated molecules. It is also noted that there is no injection of smectic properties, a common occurrence with such polar/non-polar mixtures in LMM systems [17], as well as in mixtures of polar LMM materials and polymers bearing non-polar groups [18]. The left and right hand sides of Figure 4.1 represent the transition temperatures for the pure homopolymers, and it is interesting to note that the N - I transition temperature difference for the homopolymers (47.4 °C) is much greater than that observed between the terminally cyano-substituted and terminally pentyl-substituted side chain precursor units (16.2 °C). This may suggest that pairwise correlations of polar groups are more extensive in these polymeric systems than in the low molar mass environments. Alternatively, the effects of pairwise correlations may simply be more significant for the polymer systems.

When the line joining the points for the $T_{N-I}$ values for W10 and W15 in Figure 4.1 is extrapolated, it is found to intersect the left hand axis at 7 °C. This may be regarded as an estimated N - I transition temperature for the terminal cyano-substituted homopolymer of the octyloxy series (W6) in the total absence of antiparallel correlations. Comparable results have been obtained for extrapolated $T_{N-I}$ for LMM systems [16], and these results show for the first time that the influence of antiparallel correlations on the thermodynamic properties of polymers is similar to that for LMM systems.

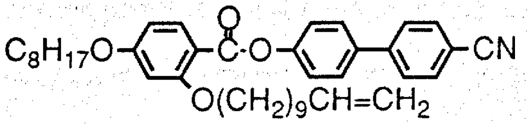
Work was then extended to include the synthesis of the side chain copolymer W16, which contains two terminally cyano-substituted side chains attached by spacers of different lengths (Figure 4.2). These results suggest that a similar behaviour is obtained. With interspersed 5- and 11- carbon spacer side chains appended along the polymer main chain, efficient antiparallel association of the cyano-groups may be more difficult to achieve, and appears to be diminished to about the same extent as that for W13.

***Figure 4.2***

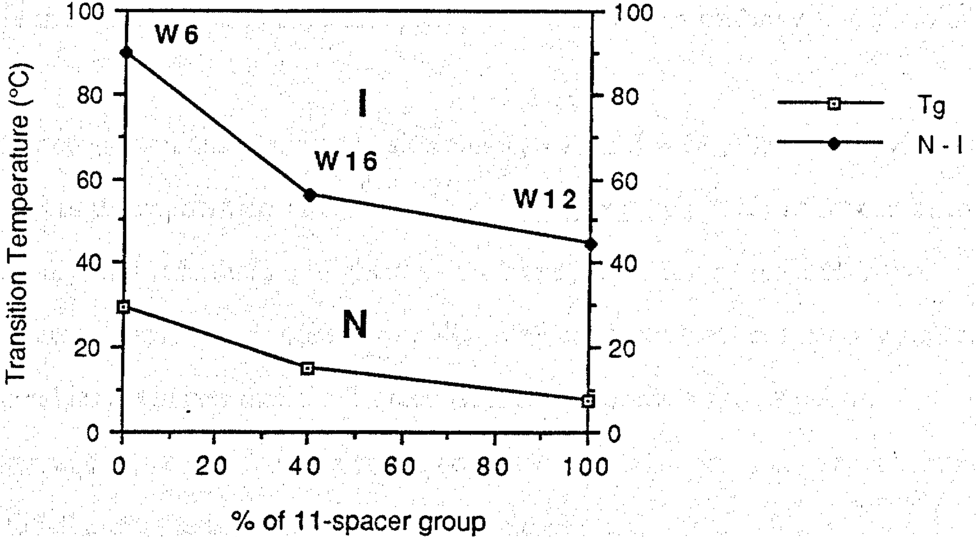
*Effect of using two different spacer lengths (5 and/or 11, precursors 5a and/or JSH), in a terminally cyano-substituted, laterally attached SCLCP*



**5a**



**JSH**



Since both side chains bear terminal cyano-groups in this case, the dielectric properties of this copolymer could be interesting, because the reduction in antiparallel correlations has been achieved without using a terminal non-polar group as diluent.

### 4.2.3 An Unusual Series Of Side Chain Copolymers

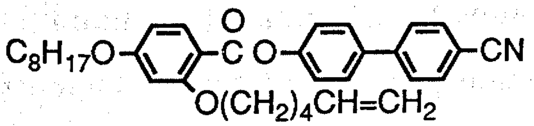
Several side chain copolymers bearing laterally attached side chains with methoxy and octyloxy groups on the left terminus of the mesogenic moiety were synthesised and found to exhibit unusual properties. The methoxy homopolymer (W4) is a purely amorphous crystalline polymer, despite the fact that the side chain precursor (**5mb**) is nematic in character. The octyloxy analogue (W9), on the other hand, is nematic up to 82 °C. With these points in mind, a range of side chain copolymers was prepared with increasing contents of methoxy side chains in order to investigate the extent to which the crystallinity of the parent methoxy homopolymer is masking its liquid crystal characteristics.

The results of this study are presented in the bottom part of Table 4.7 and in Figure 4.3. From the graph, it is apparent that the behaviour of these polymers is indeed very unique. With a 50% concentration of methoxy side chains (W20), the copolymer has a lower nematic-isotropic transition temperature, but a minimum may at first sight be indicated, because there is an increase in clearing temperature at 60% of methoxy side chain units.

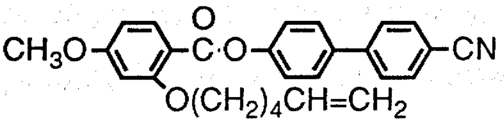
At higher concentrations of methoxy side chain (W17 and W18), the liquid crystalline properties of the copolymers are however totally extinguished. This effect occurs most dramatically, and is further highlighted by the trend shown for the glass transition temperatures. These remain constant for 40 - 60% concentrations of methoxy side chain and the values are higher than the Tg recorded for the parent octyloxy polymer. However, at a methoxy side chain content of 70%, the glass transition temperature is found to fall away sharply, again quite a dramatic effect.

***Figure 4.3***

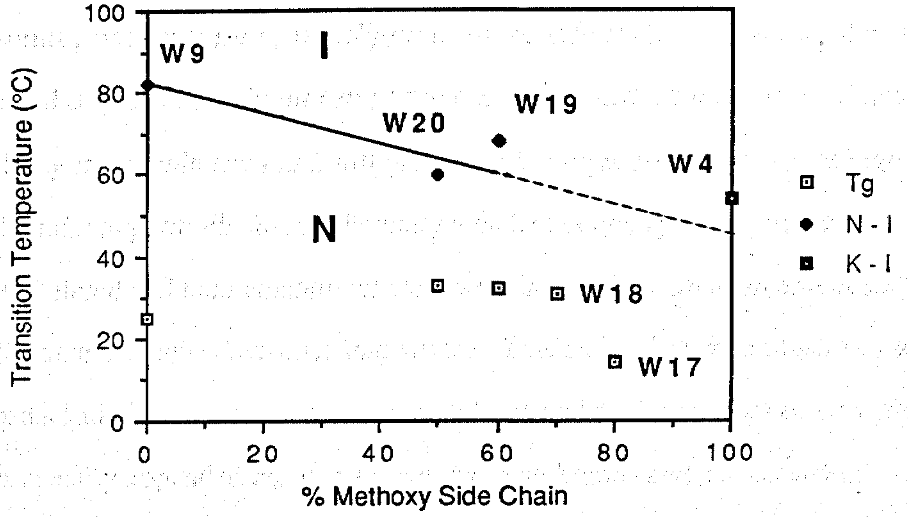
***An unusual series of side chain copolymers bearing methoxy (5mb) and/or octyloxy (5b) side chains***



**5b**



**5mb**



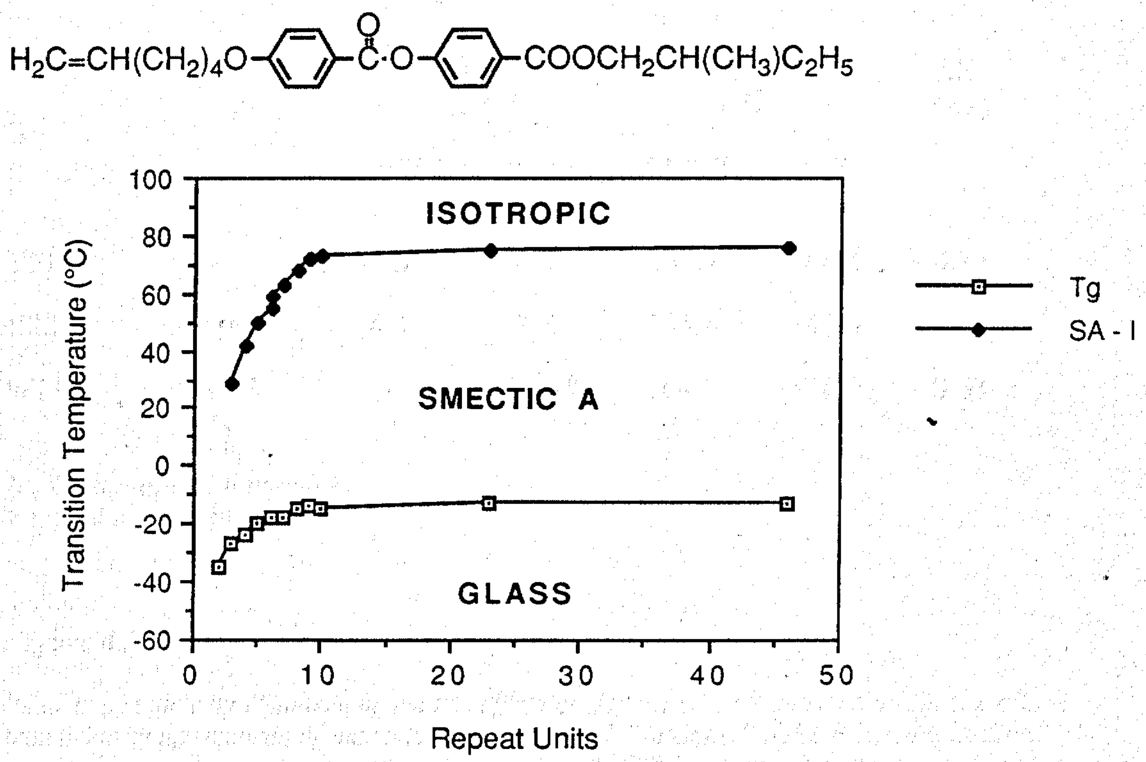
In view of these results, it is suggested that the $T_{N-I}$ increase from 50 to 60% of methoxy side chains is due to deviations from a strictly statistical distribution of side chain units. Irreproducibility, stemming from deviations from the expected ratios of side chains based on relative amounts of precursor used in the synthesis, is not believed to be a factor (see Section 4.2.6). The transition line through the $T_{N-I}$ for polymers W9, W20 and W19 is therefore drawn as a mean line and its extrapolation would indicate a monotropic $T_{N-I}$ for W4 of about 46 °C, i.e., some 8 °C below the K - I for W4. However, no nematic phase was seen in the supercooled melt. Moreover, as noted earlier, copolymers W17 and W18 show no phases and these have low Tg values, well below the $T_{N-I}$ values indicated by the extrapolated $T_{N-I}$ curve. Some quite critical factor is therefore operating at high contents of the methoxy side chain and in the methoxy homopolymer itself, such that LC properties are eliminated. It is believed that because we are dealing with a side chain with a very short alkoxy group ($CH_3O$) on the left hand side, the point of lateral attachment of the flexible spacer is very near to one end of the mesogenic group. In this situation, the side chain may behave or try to behave as a quasi-terminal side chain. With reference to the models proposed by Wang and Warner for nematic comb-like polymers [19], of which a more detailed treatment appears in Section 4.4.1, the methoxy substituted side chains would be attempting to form an oblate $N_I$ packing, whilst the octyloxy substituted side chains would try to give a prolate $N_{III}$ packing. The side chains in the methoxy substituted homopolymer are therefore appended awkwardly and are probably unable to pack and align anisotropically to form the nematic phase; hence the absence of mesomorphism in these homopolymers. In the side chain copolymers, the laterally attached octyloxy side chains can perhaps tolerate a limited population of quasi-terminal methoxy mesogenic units and still preserve LC properties. However at high populations of the methoxy side chains, the laterally attached octyloxy mesogenic groups may be overwhelmed and their anisotropic alignment interfered with to an extent such that mesophase formation becomes impossible. This series therefore illustrates some novel features and alerts us to some new possibilities and problems connected with SCLCP with laterally appended mesogenic groups, both homo- and co- polymers.

### 4.2.4 Molecular Weight Effects

Stevens *et al.* [20] had already studied the effect of degree of polymerisation on phase transition temperatures for monodisperse LC polysiloxane oligomers and polymers. Their results, which showed that only slight variations in phase transition temperatures occur for polymers which have $\overline{DP}$ values within the range 10 - 100, imply that variations in the degree of polymerisation for the preformed backbones used in this work would have only minimal effects on the thermal behaviour of the derived mesomorphic side chain polymers. However, the fractionation in the work of Stevens *et al.* was reported as having been carried out on the SCLCP after the poly(hydrosilylation) reaction. Furthermore, no factual information about the polydispersity was given, and in most cases, no polymers were examined with $\overline{DP} > 50$ (Figure 4.4). These results have since been proved to be inaccurate, for significant variations in transition temperatures have been observed by Hawthorne [21] even up to $\overline{DP} > 100$.

*Figure 4.4*

*Results of study by Stevens et al. on the effect of degree of polymerisation on phase transition temperatures*



Both Stevens *et al.* and Hawthorne conducted their work on terminally attached SCLCP. In order to corroborate the results of Hawthorne, a further two polymers were synthesised in the series worked on by Hawthorne (Table 4.8, Y21 and Y22). This was also a useful opportunity to investigate the effect of a different catalyst (PVMS), on the thermal properties of the LCP, Hawthorne having used $H_2PtCl_6$. As illustrated by Figure 4.5, these new results follow the trend shown by the earlier work. Terminally attached SCLCP have thus been synthesised using two different catalysts, but with no apparent effect on phase transition temperature, further evidence that anomalous α-addition, discussed in Section 4.2.1 for lateral appendage, is absent in terminally appended SCLCP. More significantly, the rising slope of the graph indicates that the effect of molar mass of the polymer upon the transition temperatures of the LCP is still evident at $\overline{DP}$ 100. This work has been continued at York by Hollingshurst [22], and his investigations with a different terminally attached mesogenic moiety have produced similar trends (Figure 4.6).

**Table 4.8**

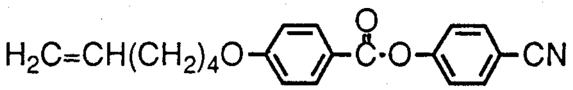
*Phase transition temperatures and enthalpies of clearing for terminally attached side chain polysiloxanes with side chain precursor 7b and made using monodisperse fractions of the PHMS backbone*

| | $\overline{DP}$ | Tg t/°C | | N - I t/°C | | ΔH cal/g |
|---|---|---|---|---|---|---|
| | | ONSET | MID-PT | ONSET | MAX | |
| Y21 | 7 | -5.3 | -4.6 | 102.9 | 108.3 | 0.74 |
| Y22 | 78 | 4.5 | 7.3 | 136.4 | 145.6 | 0.23 |
| W23 □ | 46 ± 3 | - | 45.4 K | 164.0 | 170.0 | 0.63 |

K : Crystal-smectic A transition.
□ : see discussion on p 157.

**Figure 4.5**

*Results of study by Hawthorne on the effect of degree of polymerisation on the phase transition temperatures of monodisperse terminally attached SCLCP, with additional results from polymers prepared in this work with PVMS as catalyst, bearing side chain precursor 7b*



$H_2C{=}CH(CH_2)_4O{-}C_6H_4{-}\overset{O}{\overset{\|}{C}}{\cdot}O{-}C_6H_4{-}CN$

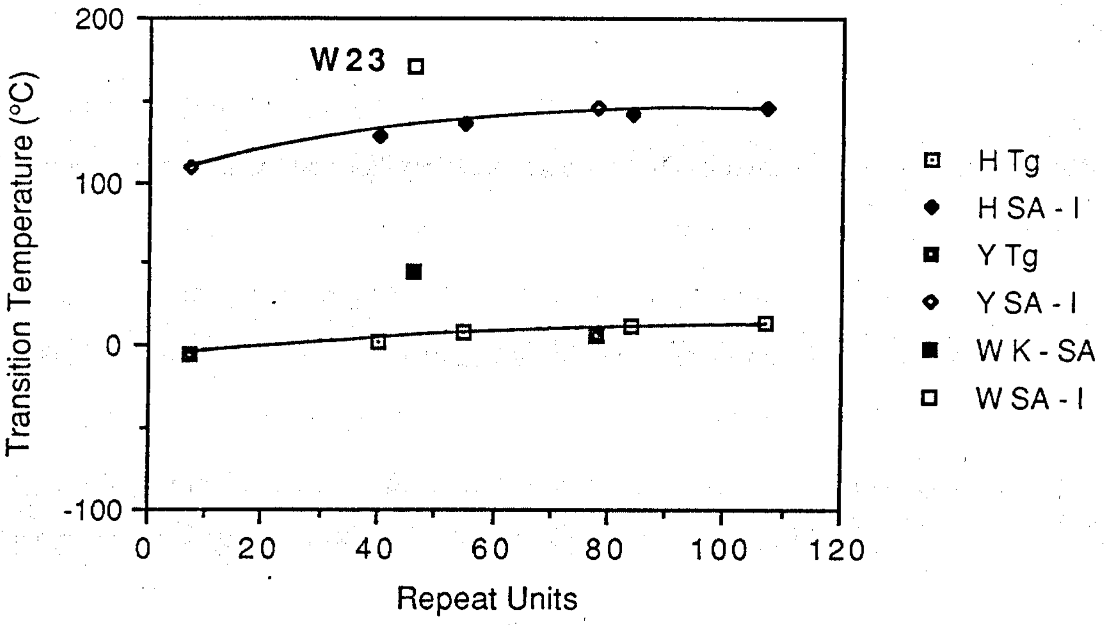
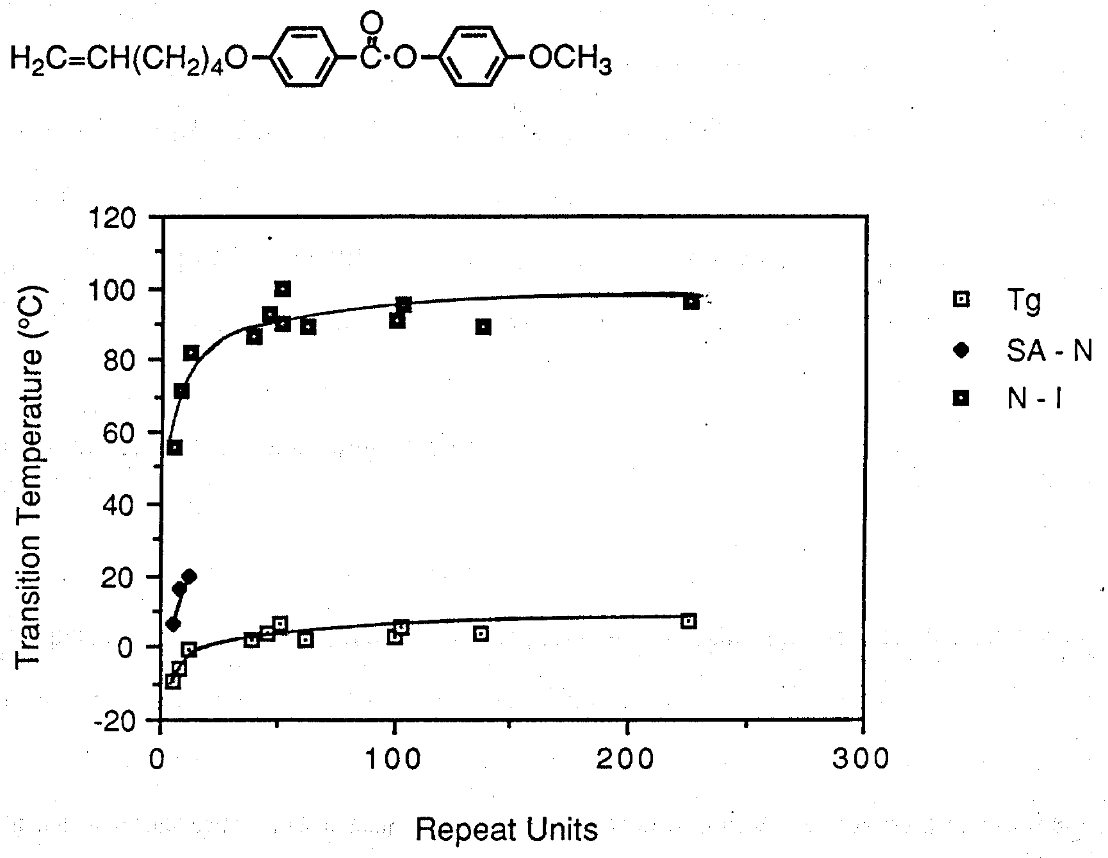


*Figure 4.6*

*Results of study by Hollingshurst on the effect of degree of polymerisation on the phase transition temperatures of monodisperse terminally attached SCLCP*



Both the nematic-isotropic transitions and the glass transition temperatures rise sharply for polymers with $\overline{DP}$ up to 20 repeat units; after $\overline{DP} = 50$, the increases become less dramatic, but they are still observable. A limiting degree of polymerisation, above which the transition temperatures remain fairly constant, is apparently reached only at about $\overline{DP}$ 100. In addition, a smectic A-nematic transition was identified for the lower molecular weight polymers. These transitions are not as pronounced on microscopic observation for the higher molar mass fractions, and they are moreover difficult to detect even by DSC. The $S_A$ - N curve could not therefore be followed after $\overline{DP} \approx 20$.

In parallel with this effort at York, an analogous study has now been made for laterally attached SCLCP. This is the first time this has been done. The side chain precursor used was 5a, and fractions of PHMS homopolymer backbone of polydispersity 1.3 or less, of known molar mass and known number of repeat units ranging from 10 to 225, were employed (Table 4.9). The poly(hydrogenmethylsiloxane) fractions, supplied by the York Polymer Group, were obtained using their careful fractionation or distillation procedures applied to polysiloxane backbone supplied by Dow Corning. These monodisperse, linear samples were characterised either by analytical gel permeation chromatography or gas liquid chromatography, followed by data evaluation using a specifically written computing package.

The first conclusion that can be drawn from these results is that the isotropisation temperature for the monomeric side chain precursor is higher than that for the lowest molar mass oligomer studied (Figure 4.7). This may be attributed to the manner in which the side chains are laterally attached to the polymer main chain, a matter already discussed in the previous section (see also Section 4.4.1). That this behaviour is contrary to that found for terminally attached systems is a further illustration of the fact that, at best, only weak increases in mesophase thermal stability and order are obtained for the laterally attached type of SCLCP, on moving from monomer to polymer [23]. In addition, the diagram shows that the N - I transition temperatures lie on a curve which rises steeply at first and appears to be continuing to rise even at $\overline{DP}$ 100. These findings provide evidence in support of Hawthorne's observations for terminally appended SCLCP that molecular weights have significant effects on liquid crystalline properties at $\overline{DP}$ values much in excess of 10 -- in fact, $\overline{DP}$ values of about 100 are required before transition temperatures become approximately constant. They of course demonstrate that continuing effects up to $\overline{DP}$ about 100 also occur for laterally appended SCLCP and emphasize the general point that legitimate comparisons of thermal data for SCLCP are only possible for comparable $\overline{DP}$ values < 100.

*Table 4.9*

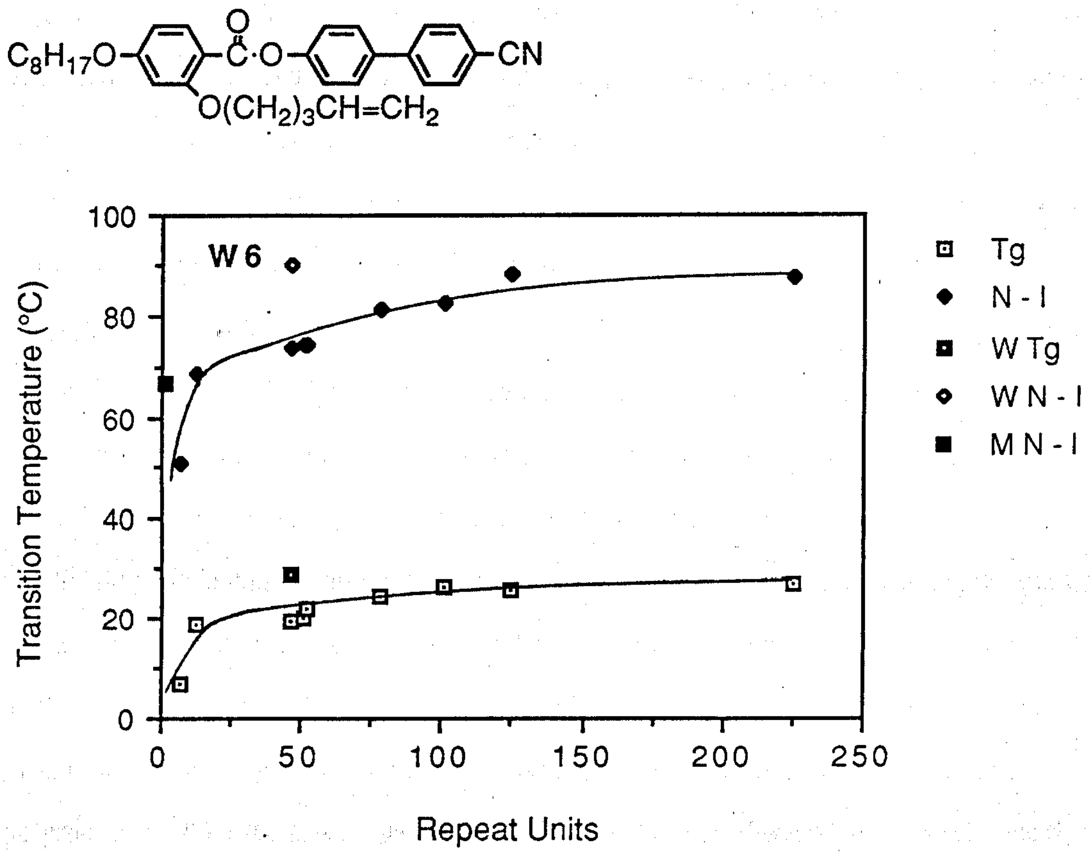
*Phase transition temperatures and enthalpies of clearing for laterally attached side chain polymers made from monodisperse fractions of poly(hydrogenmethylsiloxane) backbone and side chain precursor* ***5a***

| | | | | | Tg t/°C | | N - I t/°C | | ΔH cal/g |
|---|---|---|---|---|---|---|---|---|---|
| | $\overline{Mw}$ | $\overline{Mn}$ | $\gamma$ | $\overline{DP}$ | ONSET | MIDPT | ONSET | MAX | |
| Y24 | - | 582 | 1.00 | 7 | 6.0 | 7.0 | 49.6 | 50.8 | 0.13 |
| Y25 | - | 942 | 1.00 | 13 | 16.5 | 18.6 | 67.2 | 68.7 | 0.16 |
| Y26 | 4201 | 2948 | 1.43 | 46 | 19.3 | 19.6 | 70.5 | 73.3 | 0.14 |
| Y27 | 3867 | 3225 | 1.20 | 51 | 19.8 | 20.2 | 71.3 | 74.0 | 0.17 |
| Y28 | 3673 | 3291 | 1.12 | 52 | 19.2 | 21.7 | 69.7 | 74.1 | 0.19 |
| Y29 | 5201 | 4862 | 1.07 | 78 | 24.5 | 24.6 | 78.2 | 81.0 | 0.19 |
| Y30 | 6491 | 6224 | 1.04 | 101 | 24.8 | 26.4 | 79.4 | 82.5 | 0.18 |
| Y31 | 7991 | 7641 | 1.05 | 125 | 23.6 | 25.5 | 82.1 | 88.0 | 0.31 |
| Y32 | 14123 | 13664 | 1.03 | 225 | 25.3 | 26.8 | 82.8 | 87.4 | 0.26 |
| W6 ¤ | - | 2920 | 2.30 | 46 | 28.7 | 29.4 | 84.6 | 89.8 | 0.24 |

¤ : see discussion on p 157.

*Figure 4.7*

*Effect of molecular weight on the liquid crystalline properties of monodisperse laterally attached side chain polysiloxanes bearing side chain precursor 5a*



In all of the systems examined, the glass transition temperatures within a series of polymers have been found to rise with increasing chain length. This is related mainly to the presence of the end-groups, which tend to create a large free volume in the polymer compared to the main chain segments. With shorter chain lengths, the concentration of chain-ends is more dominant, and this increases the effective free volume of the polymer. This causes the significantly lower glass transition temperatures that are observed in the lower molecular mass polymers. As the chain lengths increase, intermolecular interactions become possible and reduce the free volume. Ultimately, a limiting degree of polymerisation is reached at which the intermolecular and intramolecular interactions are in equilibrium, and above which the free volume remains approximately constant. This limiting degree of polymerisation has been suggested to be *ca.* 75 - 100, whereon the glass transition temperatures become approximately constant [24]. From the examples shown in Figures 4.5, 4.6 and 4.7, this claim of a limiting Tg value, as a function of $\overline{DP}$, occurring in the $\overline{DP}$ range proposed appears justifiable. By analogy, the above reasoning and constraints should also be applicable to the mesomorphic properties. The extent of side chain interactions should increase with backbone length ($\overline{DP}$), and therefore raise the clearing temperature, but obviously again, only up to some limiting value. A plot of isotropisation temperature against molar mass would therefore be expected to rise steeply at first and then level at $\overline{DP}$ 75 - 100, as in fact observed.

The polydispersity of polymers is also known to affect liquid crystalline properties [21]. Hawthorne observed that increases in the heterogeneity index reduce both the glass transition and clearing temperatures of SCLCP. This has been interpreted as a plasticising effect caused by the low molar mass species present in the homogeneous mixture and which contribute to the broad distribution of the polymer molecular weight. The thermal behaviour observed is in fact similar to that reported by Finkelmann *et al.* for mixtures of liquid crystal polymers and low molar mass mesogens [11]. The dilution of polymer chains, by the low molar mass oligomers, has the effect of reducing the local viscosity coefficient for the chain segments. This allows the segments to rotate more freely, increases the free volume of the material, and thereby lowers the glass transition temperature. Similarly, the dilution effect of the oligomers is able to influence the overlap and ordering of the side chains, and this suppresses the clearing temperature.
In addition, such a mixture of molar masses causes a broadening of the temperature range over which isotropisation occurs -- *cf.*, the biphasic gap observed at $T_{cl}$ for mixtures of LMM materials. With a variety of low and high molar mass chains, a series of transitions at different temperatures would result in a wide thermal profile being detected.

The effect of polydispersity was then investigated for both the terminally and laterally attached systems previously studied, by appending the respective side chains onto commercially available Wacker poly(hydrogenmethylsiloxane) backbone, known to have a fairly broad polydispersity of 2.3. The relevant results have been included in Tables 4.8 and 4.9, and Figures 4.5 and 4.7. The polymers are numbered W23 and W6.

In both cases, the transition temperatures are considerably higher than the maximum clearing temperatures recorded for the monodisperse polymers with up to 225 repeat units, despite the fact that the Wacker backbone used has a $\overline{DP}$ of only 46. It is believed that the higher molecular weight chains present in the broadly distributed polymer must have a strongly dominant effect upon the thermal properties, in accordance with the proposal by Sagane and Lenz [25]. Tg values are also affected in a similar manner.

The molar mass of a polymer may be related to the temperature of its glass transition *via* a number of possible mathematical expressions. Fox and Flory suggest a plot of Tg(m), the value of the glass transition in Kelvin measured at a molar mass (m), against the reciprocal number-average molar mass [26]. The y-ordinate intercept allows the estimation of Tg(∞), the temperature of the glass transition of the polymer at infinite molar mass (Figure 4.8). An alternative approach, proposed by Ueberreiter and Kannig considers the linear dependence of the glass transition temperature upon reciprocal molar mass [27]. By re-arranging their equation, is is possible to plot $\overline{Mn}$/Tg(m) against $\overline{Mn}$; the gradient of the slope is then equivalent to $[Tg(\infty)]^{-1}$ (Figure 4.9). The results from the present study of laterally attached SCLCP have been plotted using both relationships, in order that the corresponding values for Tg(∞) may be obtained. It has been possible to obtain these data only because of the availability of well characterised, sharp fractions of poly(hydrogenmethylsiloxane), obtained by preparative gel permeation chromatography. The interpolated Tg(∞) value is found to be 299K by the Fox-Flory method, and this compares very favourably with the result obtained using the Ueberreiter-Kannig technique, which gives the glass transition temperature at infinite mass as 300K.
The extrapolated value from the experimental data used to obtain Figure 4.7 is *ca.* 27 °C (300K), agreeing well with these values.

*Figure 4.8*

*Glass transition temperature versus reciprocal number-average molar mass for the laterally attached SCLCP, using the Fox and Flory expression*

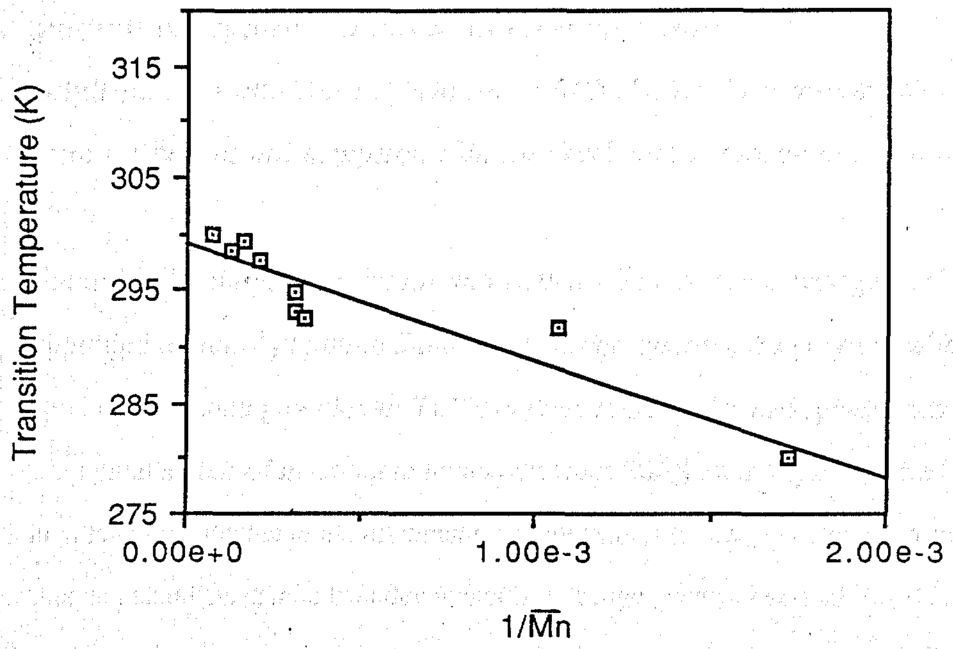
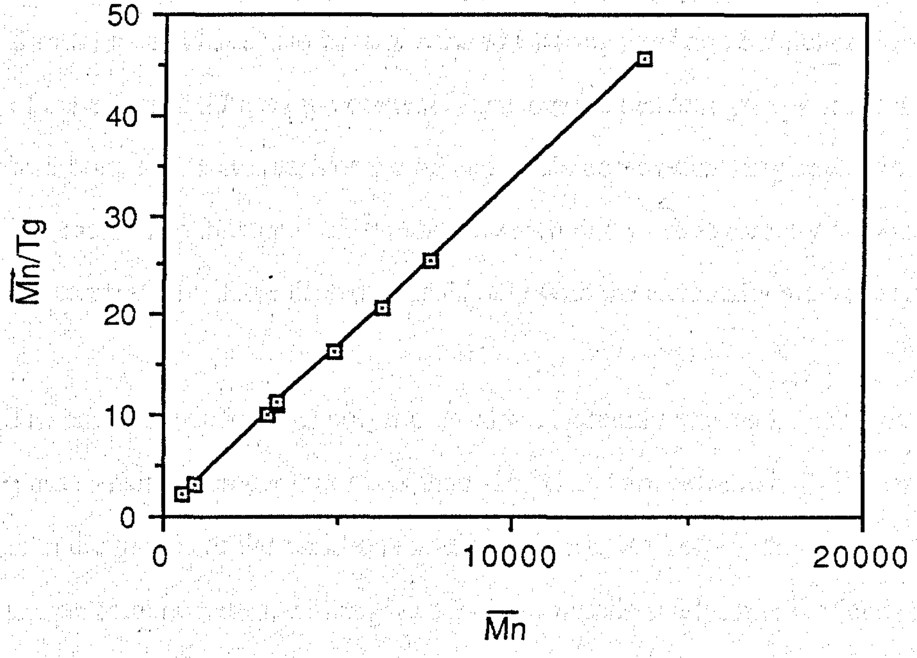


*Figure 4.9*

*($\overline{Mn}$/Tg) versus $\overline{Mn}$ for the laterally attached SCLCP, using the Ueberreiter and Kannig expression*



### 4.2.5 Backbone Copolymers

In an attempt to examine the effect of changing backbone flexibility on phase transition temperatures, laterally attached SCLCP, derived from the poly(hydrogenmethyldimethylsiloxane) [P(HM/DM)S] backbone supplied by Petrarch, were synthesised and compared with their backbone homopolymer analogues.

Frenzel and Rehage have already shown that when the same mesogenic side chain is appended terminally to three different backbone systems, the polymer with the more flexible backbone gives lower Tg/Tm values and broader mesophase ranges [28]. This greater ease of mesophase formation from the glass or crystal phase is accompanied however by a decrease in isotropisation temperatures, i.e., a decrease in mesophase thermal stability. Since broader mesophase ranges were observed, the decrease in Tg/Tm is obviously greater than the decrease in the isotropisation temperature. The decrease in mesophase thermal stability with increasing backbone flexibility must be a complex issue; the side chains should be freer to align anisotropically, but the backbone will contribute less to the maintenance of this order. Backbone rigidity must also affect the manner in which the side chains pack together, and hence the type of mesophase that is formed. Similar results have also been generated by Ringsdorf and Schneller from investigations of the effect of diluting the content of mesogenic pendent groups along a P(HM/DM)S backbone [29]. However, like the related publication which originated from these laboratories by Nestor *et al.* [30], and to which this work is directly comparable, the currently available literature deals only with the terminally attached type of SCLCP.

The backbone copolymer polysiloxanes with laterally attached mesogenic groups all have glass transition temperatures less than -10 °C and are extremely fluid -- much less viscous than the phases of the backbone homopolymers. As before, the polymers are room temperature nematics, which give the characteristic sandy, fine schlieren texture of the nematic phase. These nematic textures are assumed immediately without annealing. The difference in backbones has not therefore affected the phase type, but significant reductions in transition temperatures have been observed -- these are recorded in Table 4.10. Through the synthesis of this novel series of laterally attached SCLCP from the copolymer backbone, a range of room temperature nematics offering alternative operational mesomorphic properties to their homopolymer analogues has therefore been prepared.

Before any conclusions can be drawn about the differences in transition temperatures for the backbone homo- and co- polymers, allowance must first be made for the appreciable difference in the degree of polymerisation between the two backbones. The $\overline{DP}$ of the PHMS backbone used was 46, while the $\overline{DP}$ for the P(HM/DM)S backbone was 13 (26 Si in the backbone), and in the previous section, attention has been drawn to the fact that phase transition temperatures are significantly affected by both the degree of polymerisation and polydispersity of the polymers. The difference in $\overline{DP}$ for the two polymer backbones must therefore be taken into consideration, before attempting to interpret the results obtained for the two series of SCLCP in any other terms.

With reference to the graph (Figure 4.7), an estimated N - I transition value for a laterally attached SCLCP made from a PHMS homopolymer backbone, with the same number of mesogenic groups along its backbone as that for the P(HM/DM)S copolymer backbone, i.e., 13 mesogenic groups, can be obtained. This figure is 68.6 °C, and when compared to that recorded for the copolymeric analogue (36.6 °C), is still 32 °C higher. Since the variable parameter of differing degree of polymerisation has now been allowed for, this suggests that a further factor must be considered to explain the fact that the N - I transition temperature predicted from the plot is larger than the observed value. This discrepancy must be a consequence of the decrease in backbone flexibility, on passing from the copolymer backbone to the homopolymer backbone, in which every Si atom carries a bulky mesogenic group. By 'diluting' the mesogenic groups along the main chain with non-mesogenic segments, the interactions between the large mesogenic groups, which stiffen the backbone and restrict its freedom to adopt random configurations, are reduced [29]. This accounts for the marked reductions in transition

*Table 4.10*

*Phase transition temperatures and enthalpies of clearing for laterally attached side chain homopolymers and copolymers on the backbone copolymer*

| | Alkenes mol-% | | | | Tg t/°C | | N - I t/°C | | ΔH cal/g |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | ONSET | MID-PT | ONSET | MAX | |
| P33 | 5a | 100 | 5c | 0 | -14.5 | -12.5 | 31.4 | 36.6 | 0.09 |
| P34 | 5a | 60 | 5c | 40 | -14.2 | -13.8 | 26.8 | 28.5 | 0.09 |
| P35 | 5a | 50 | 5c | 50 | -17.4 | -16.8 | 22.3 | 23.8 | 0.10 |
| P36 | 5a | 40 | 5c | 60 | -20.7 | -16.6 | 23.7 | 24.9 | 0.12 |
| P37 | 5a | 0 | 5c | 100 | -23.5 | -22.0 | 22.8 | 23.6 | 0.21 |

temperatures for the polymers with the flexible P(HM/DM)S backbone. Indeed, the highly flexible backbone may be able to distribute itself throughout the anisotropic alignment of the side chains, in a manner that would not be possible for the homopolymer systems. In fact, it is noted that the increased backbone flexibility has not only reduced transition temperatures, but has also acted against the molecular ordering in the nematic phase. This can be inferred from the reduced enthalpy values for the backbone copolymer systems (Table 4.11). For terminally attached SCLCP, it has been shown that despite decreased transition temperatures, the ΔH values of smectic to nematic or isotropic transitions are larger for the backbone copolymer than for the homopolymers [30]. Nestor *et al.* again interpreted this in terms of backbone flexibility. The flexible polysiloxane backbone is suspected here of being accommodated between the smectic layers. This makes possible a high degree of smectic order of the side chains, which would warrant a larger enthalpy value in the case of the backbone copolymers, compared to the more rigid homopolymer backbone systems, where the side chains are not allowed to pack as efficiently. However, Nestor *et al.* observed the converse enthalpy effect to occur for the nematic to isotropic transition, but this was for just one polymer. However, the result is in agreement with these findings for lateral systems.

*Table 4.11*

*Differences in phase transition temperatures and enthalpies of clearing between the two series of polymers (W) and (P) [Table 4.7 - Table 4.10]*

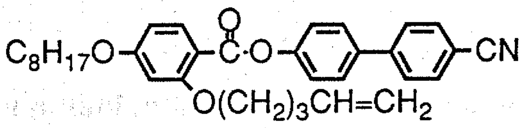
| Difference | $\Delta'Tg$ t/°C | $\Delta'N - I$ t/°C | $\Delta'(\Delta H)$ cal/g |
|---|---|---|---|
| W6 - P33 | 41.9 | 53.2 | 0.15 |
| W13 - P34 | 31.9 | 24.2 | 0.06 |
| W14 - P35 | 22.5 | 14.1 | 0.06 |
| W15 - P36 | 12.0 | 3.1 | 0.03 |
| W10 - P37 | 23.2 | 18.8 | 0.24 |

As the laterally attached SCLCP synthesised exhibit only nematic phases, due to the manner in which the side chains are attached to the polymer backbone [31], it has not been possible to substantiate the observations of Nestor *et al.* for smectic phase transitions.

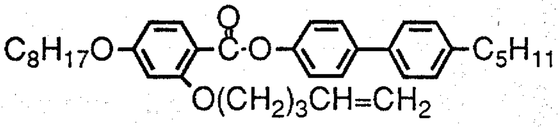
In Section 4.2.2, the effect of polar lateral group dilution by non-polar lateral groups attached to the PHMS homopolymer backbone was discussed. As shown in Figure 4.1, a strong deviation from a linear dependence is observed with increasing non-polar content. This suggested that a decrease in antiparallel pairwise correlations between cyano-groups had been achieved by such a dilution [16]. This study was then repeated to see the effect of a similar dilution, but for the P(HM/DM)S copolymer backbone. From Figure 4.10, it is seen that no real minimum in the plot is distinguishable; the mean $T_{N-I}$ line shows only a slight concavity. This result may not be surprising when it is considered that there is statistically a smaller chance of pairwise correlations occurring in a system that has already been diluted by non-polar entities (i.e., the Me groups on the backbone). As not every Si is carrying a mesogenic side chain, regardless of whether it bears a terminal polar or non-polar group, the inference is that the effect of dilution is not as dramatic as before, and that antiparallel pairwise correlations do not play such a major role in these copolymer backbone systems.

***Figure 4.10***

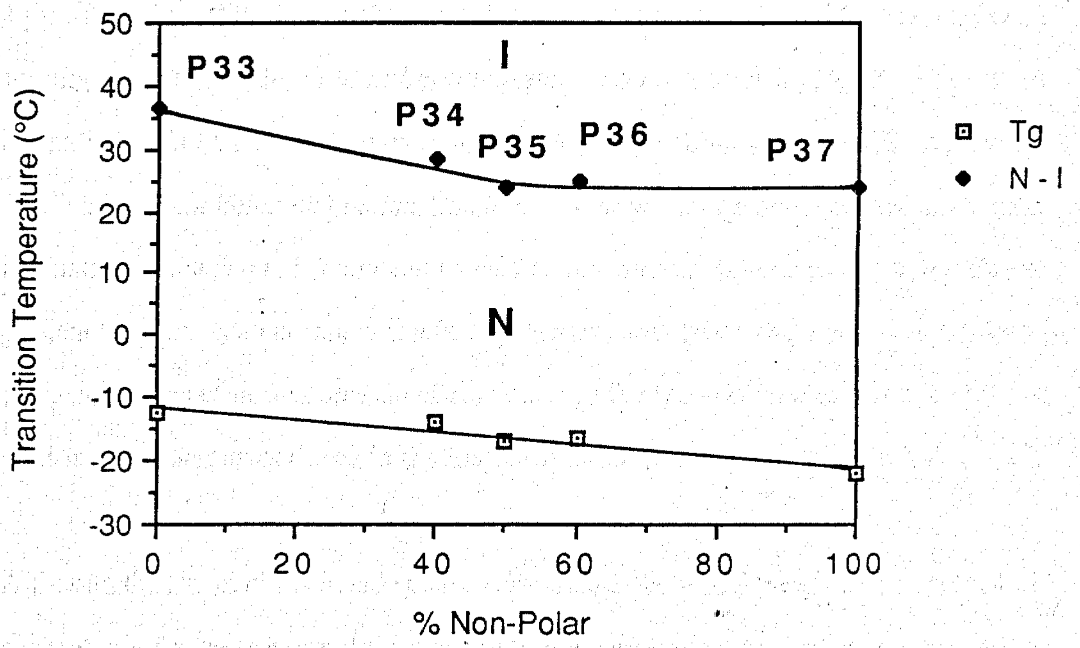
*Effect of terminal polar group (5a) dilution by terminal non-polar groups (5c) attached to the P(HM/DM)S copolymer backbone*



**5a**



**5c**



### 4.2.6 Side Chain Ratios and Polymer Miscibility

For all side chain copolymers synthesised, it was necessary to check the ratio of side chains actually achieved. As the preformed backbone had been exposed to a 10 mol-% excess of each alkene, the final ratio may deviate appreciably from that used in the reaction feed-stock, e.g., if factors such as steric hindrance and different degrees of reactivity of the precursor mesogenic units have a significant effect on the kinetics of the hydrosilylation. The side chain percentages were determined by $^1$H NMR and were remarkably close to the expected percentages -- no more than 1 - 3% of an excess in contribution from the terminal cyano-substituted side chain was normally observed. The integrals for benzylic protons (exclusive to side chain **5c**) and for the combined aromatic peak at $\delta = 6.5$ (common to side chains **5a** and **5c**) were used to obtain the percentage side chain composition in copolymers with polar and non-polar groups; the percentages of non-polar side chain compared to those estimated from the feed-stocks of side chain precursors used in the hydrosilylation process are given in Table 4.12.

Although the fluctuations in side chain composition between the expected and calculated percentages for these examples were small, the copolymers had to be assumed to be statistical in nature, and it was expected that transition temperature reproducibility would be difficult to achieve from batch to batch, due to local variations in side chain population on individual backbones within the bulk sample. In view of the potential value of such copolymers, the desirability of achieving batch consistency is obvious.

*Table 4.12*

*Calculated percentages of side chain in copolymers of the PHMS series (W) and the P(HM/DM)S series (P), compared to the feed-stock percentages of side chain precursors used*

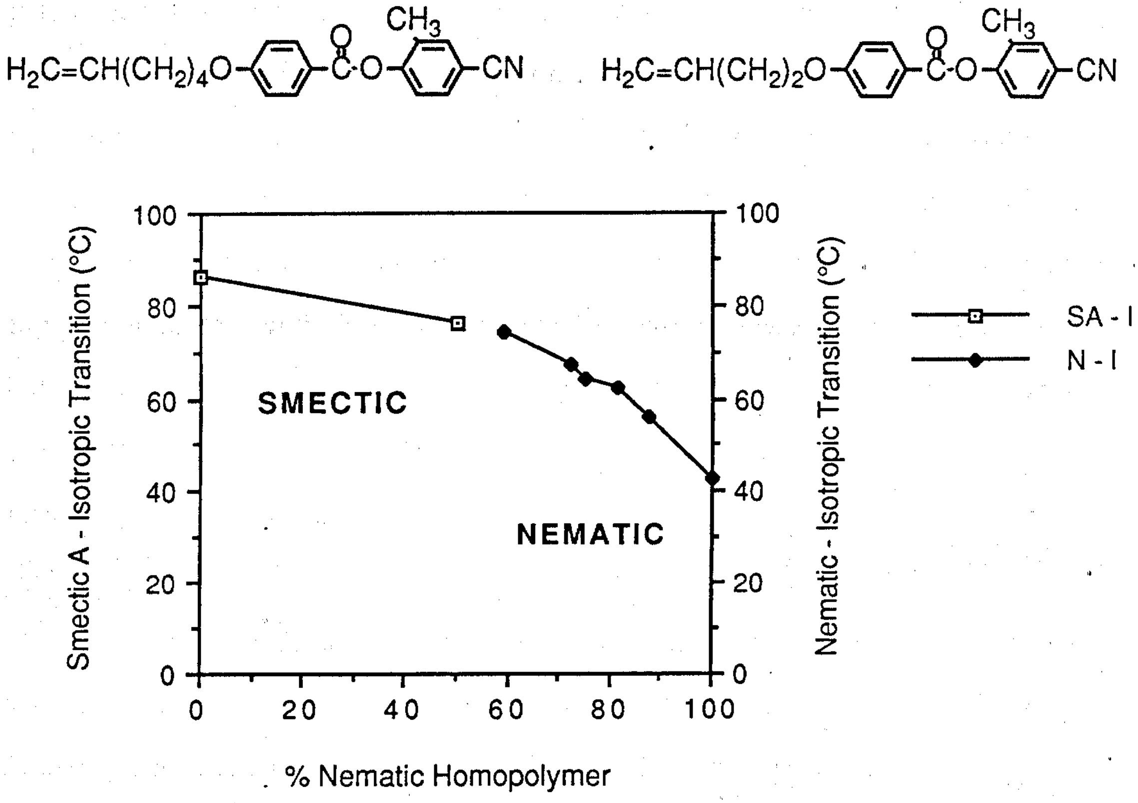
| | Benzylic protons (integral) | Peak at $\delta = 6.5$ (integral) | Terminal-pentyl side chain, 5c % (calc. from NMR) | % (expected) |
|---|---|---|---|---|
| *Hompolymer backbone (W)* | | | | |
| W13 | 1 | 2.63 | 38 | 40 |
| W14 | 1 | 1.96 | 51 | 50 |
| W15 | 1.17 | 1.99 | 59 | 60 |
| *Copolymer backbone (P)* | | | | |
| P34 | 1 | 2.33 | 43 | 40 |
| P35 | 1 | 2.10 | 48 | 50 |
| P36 | 1.14 | 1.92 | 59 | 60 |

In LMM liquid crystalline materials, the fine tuning of properties such as viscosity, phase type, transition temperature, elastic constants etc. is conveniently achieved by the mixing of components. If different side chain polymers were co-miscible, a solution to the above problem of reproducibility would be to prepare accurate physical mixtures of polar and non-polar homopolymers, each separately carrying the desired mesogenic groups. This would guarantee that consistency of composition was achieved, and the mixtures might emulate the desirable properties obtained from mixed lateral/terminal copolymers (see Section 4.4).

There is, however, some debate as to whether structurally different or even similar side chain liquid crystal polymers can be miscible. It was believed that at least some SCLCP could be miscible as a result of some experimental observations by Nestor in 1985 [32]. Here, both side chain homopolymers terminated in cyano-groups and full miscibility was found right across the binary diagram of state. The results are shown in Figure 4.11.

*Figure 4.11*

*Results of a study by Nestor of the miscibility of two polysiloxanes bearing terminally attached side chains with cyano-groups at the terminus*



The original binary mixtures used by Nestor were found and re-examined in this work; the transition temperature data were correct, and segregation had not apparently occurred even after the mixtures had been left to stand for four years. In this case, the antiparallel correlations between cyano-terminated side chains may have played a role in promoting miscibility.

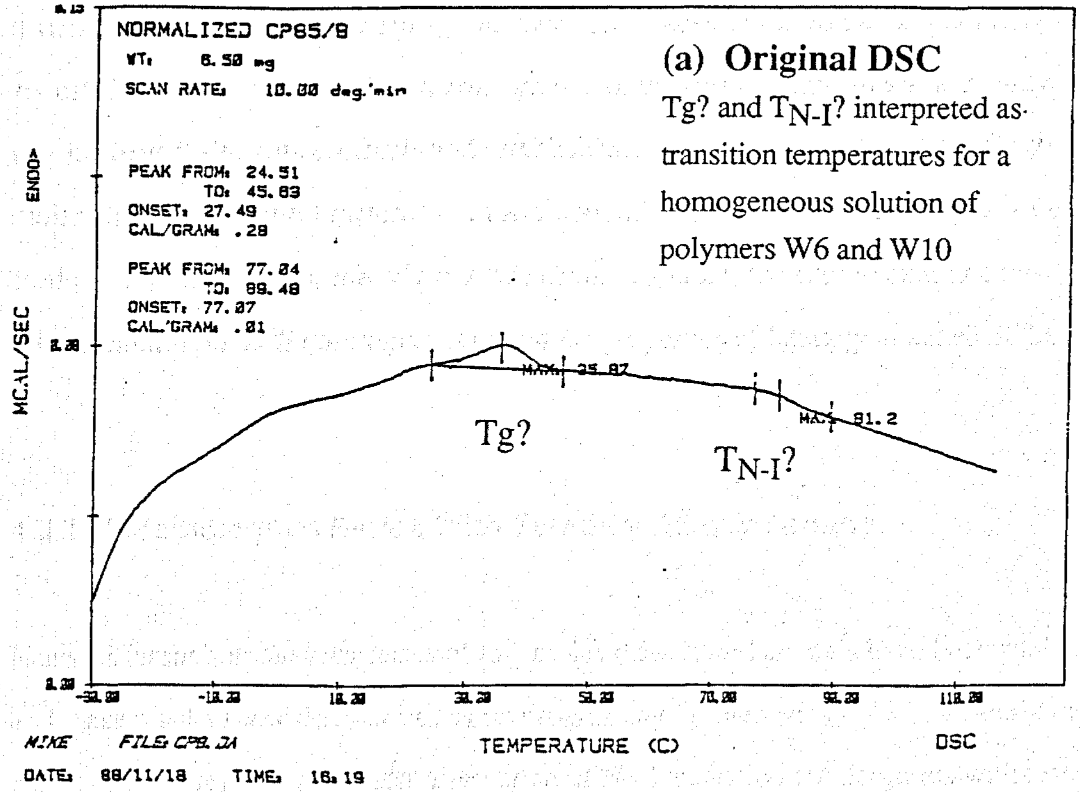
The general position seems to be that most SCLCP are mutually immiscible; miscibility certainly cannot be assumed, and has to be checked out for each system that may be of interest. It was initially thought that physical mixing for two of the present laterally attached side chain homopolymers, one bearing terminal cyano-groups (W6) and one bearing terminal pentyl-groups (W10), in ratios analogous to those used in the side chain copolymers synthesised, had occurred and given mixtures with phase transitions (glass and isotropisation) intermediate between those of the two pure components

(Figure 4.12a). However, on careful re-examination, it emerged that the true situation was one intermediate between the two extremes of total miscibility and immiscibility, i.e., partial mixing of the two homopolymers bearing side chains with markedly different chemical structures (one polar, the other non-polar) was probably occurring, a phenomenon also observed by Ringsdorf *et al.* for mixtures of polymeric and low molar mass liquid crystals [33]. However, the situation was found to be time dependent, since a clear separation of the two polymers in the mixture, giving rise to two nematic and two glass transitions with similar phase transition temperatures to the respective homopolymers, became apparent with time (Figure 4.12b). This coexistence of two sets of phases was established by differential scanning calorimetry and confirmed by microscopic observations.

It appears then that under some circumstances, two side chain polymers can be miscible, but in other cases they are not. Also, contrary to mixtures of low molar mass derivatives, demixing often occurs for mixtures and solutions of isotropic polymers [34, 35]. Ambrosino and Sixou [36], working with hydroxypropylcellulose and its partially and fully acetylated derivatives have found that miscibility depends upon the degree of acetylation. Hardouin *et al.* suggest that partially substituted side chain polysiloxanes, i.e., backbone copolymers, are more efficient in promoting miscibility compared with cases of totally substituted or unsubstituted backbones [18]. Other researchers have also found that even when considering mixtures of side chain polymers and low molar mass LC, total miscibility cannot be assumed to be the rule [37, 38]. Difficulties that arise in the mixing of polymers therefore severely limit the possibilities for tuning polymer properties by this technique. However, despite all these difficulties, the making of physical mixtures of SCLCP remains of great interest and certainly merits further attention.

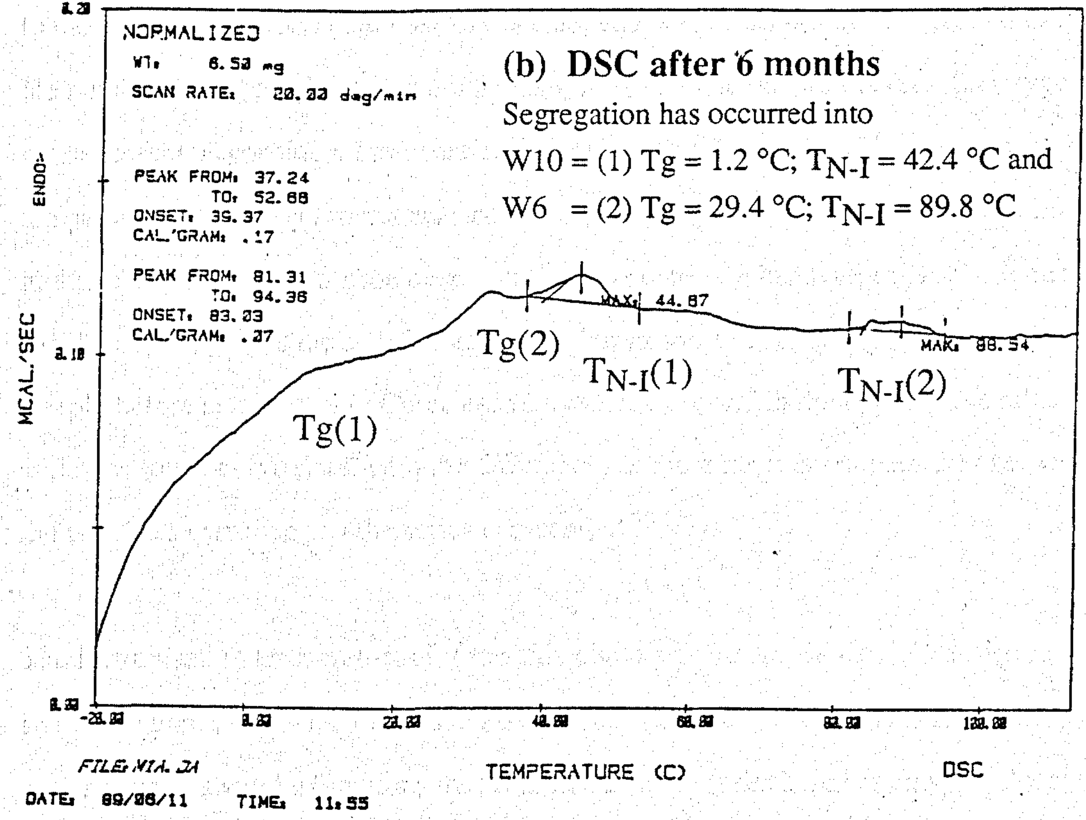
*Figure 4.12*

*DSC results for a physical mixture of two laterally attached SCLC homopolymers bearing terminal polar (W6) and non-polar (W10) groups, in a 60:40 ratio of W6 to W10*



**(a) Original DSC**

Tg? and $T_{N-I}$? interpreted as transition temperatures for a homogeneous solution of polymers W6 and W10



**(b) DSC after 6 months**

Segregation has occurred into

W10 = (1) Tg = 1.2 °C; $T_{N-I}$ = 42.4 °C and

W6 = (2) Tg = 29.4 °C; $T_{N-I}$ = 89.8 °C

## 4.3 STRUCTURE-PROPERTY CORRELATIONS

In order to develop more secure structure-property correlations, a range of polymers with a variety of end-groups has been synthesised. This work included the preparation of a series of polymers with terminal alkoxy groups of different lengths to allow a study of any 'odd-even' alternation effects and establish how any trends relate to those for low molar mass liquid crystal materials. In addition, minor structural modifications were made to the 'template' for the original side chain precursor, in order to examine the effects of changes to the mesogenic core on the properties of laterally attached SCLCP.

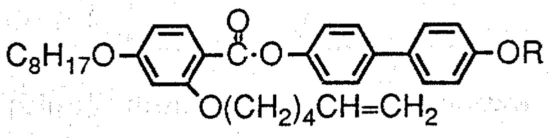
### 4.3.1 A Homologous Series With Terminal Alkoxy Groups

Many different homologous series of low molar mass liquid crystals have been studied, and these results show distinct trends on progressing up the series [15]. For a family of nematogens, a regular 'odd-even' alternation of N - I transition temperatures with respect to the length of the alkyl chain usually occurs, and when these values are plotted against the number of carbons in the terminal chain, the points lie on two curves. An oxygen, when present, is considered to exercise the effect of a $CH_2$ group. The transition temperatures for the odd members (inclusive of any oxygen) are then found to lie on a higher curve than those for the even members. A common behaviour is for both curves to fall and level off as the series is ascended, but in some cases both curves may rise steeply before levelling out. Cases are also recorded in which the upper curve falls, while the lower curve rises, with the differences in the transition temperatures between the two lines narrowing as the series is ascended [39].

The isotropisation temperatures for the side chain precursors, **5e - n**, i.e., a series of side chain precursors with terminal alkoxy groups (OR) and bearing a lateral chain terminating in a vinylic function, are given in Table 4.1 (reincluded as an appendix at the end of this section for convenience) and plotted against number of carbons in R in

***Figure 4.13***

*'Odd-even' alternation effect for a homologous series with terminal alkoxy groups*



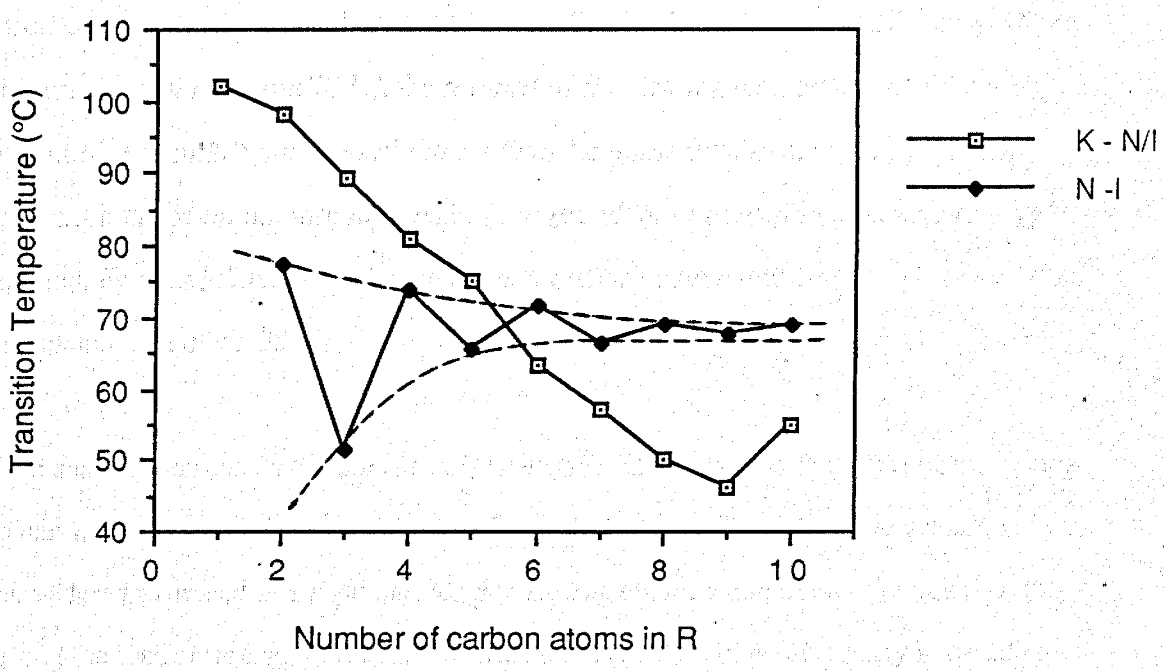


Figure 4.13. It can be seen that the distribution of the points takes the last form mentioned above, with the even carbon chain members having higher nematic-isotropic transition temperatures than the odd members. Furthermore, the alternation in the transition temperature damps out, i.e., is greatest for the lower members of the series and then gradually diminishes and becomes less pronounced for the higher homologues, as seen by the more constant N - I transition temperatures obtained for the members $OC_7$ - $OC_{10}$.

The melting points, however, do not show a regular alternation effect, but merely fall with increasing alkyl chain length, with the exception of $OC_{10}$ for which the melting point rises again. The lower members of the series exhibit a monotropic nematic phase, but the phases change to being enantiotropic when the end-group is $OC_6$. By extending the length of the terminal group, the anisotropy of molecular polarisability is maintained roughly constant for the odd carbon chain members and is increased markedly for the even homologues. As a consequence, the nematic thermal stability stays about the same or is increased and the 'cross-over' is observed as a result of the steadily falling melting points from those of the early homologues. Another outcome of the high melting points for the lower homologues is that the value of the N - I transition temperature for the methoxy derivative **5e** could not be detected. Due to the onset of crystallisation, which occurred rapidly at about 70 °C, the reversal of the clearing temperature could not be obtained, although it was possible to confirm the phase type as nematic by quench cooling and optical microscopy. At best, a 'virtual' N - I transition temperature may be quoted, by extrapolating the plot for the odd carbon chain members; this gives an estimated $T_{N\text{-}I}$ of *ca.* 35 °C.

The shapes assumed by the curves may be explained in terms of the effect of increasing chain length on the anisotropy of molecular polarisability [40]. If the alkoxy chain is considered to extend as a rigid and regular zig-zag chain, the increment in polarisability along the molecular long axis is about twice the increment in polarisability perpendicular to the axis on passing from an odd to an even carbon chain member. The polarisabilities along and perpendicular to the long axis are however increased almost equally on passing from even to odd carbon chain member. As such, the anisotropy of molecular polarisability is greater for the even carbon chain member, and this is reflected in their higher N - I transition temperatures. However, as the chain lengths increase, the statistical population of non-extended conformations increases and gives a progressive decrease in the differences in anisotropy of molecular polarisability between odd and even members; this leads to the observed damping of the alternation in the N - I transition temperatures with the higher homologues. Although these arguments have been applied to explain the observed effects, strictly speaking they are only applicable to rising types of transition temperature curve, since they are based on assumptions that the anisotropy of molecular polarisability increases along the homologous series. Other factors involving entropy, packing effects, and steric intermolecular repulsions are also important and must be considered in more generalised treatments of such effects.

For the laterally attached SCLCP, the glass transition temperatures fluctuate only marginally on ascending the series (Figure 4.14), but in an approximate 'odd-even' fashion. The methoxy derivative W38 now exhibits an enantiotropic nematic mesophase from the Tg until a temperature of 60.6 °C, i.e., the tendencies for crystallisation have been suppressed. Reference to Figure 4.13 reminds us of the very low $T_{N-I}$ for the terminal methoxy side chain precursor. The $T_{N-I}$ for the SCLCP occurs however at a much higher temperature than might have been expected, based upon earlier trends noted on passing from side chain precursor to laterally appended SCLCP. One concludes therefore that the methoxy group is too short to promote the mesomorphic properties of the side chain precursor carrying its bulky side substituent, but when this side chain is attached to the backbone, the terminal methoxy group compares favourably with other longer alkoxy groups with regard to stabilisation of the mesophase. Because of the higher transition temperatures (N - I) for the side chain precursors with longer terminal alkoxy groups, the novel effect noted earlier in Section 4.2.2 (see Appendix to Section 4.3 and Table 4.13) for side chains bearing terminal groups of low polarity is observed, i.e., the $T_{N-I}$ values are <u>lower</u> for laterally appended SCLCP compared to the corresponding monomer. The above observations emphasize however that, overall, it is unwise to make sweeping generalisations about the effects upon mesophase thermal stability on passing from side chain precursor to SCLCP.

Figure 4.14 shows that although the $T_{N-I}$ values for the SCLCP exhibit some degree of regularity as the alkoxy group is lengthened, the 'odd-even' effect is far from being perfect. A number of points deviate from the idealised plot, the $OC_4$ and $OC_6$ polymers in particular having $T_{N-I}$ values lower and higher, respectively, than expected, and this highlights the problem of achieving consistency and reproducibility of thermal data for polymer preparations. A number of factors may be responsible -- residual side chain precursor which may have escaped detection by TLC in the final 'cleaned' polymer (although this seems unlikely), incomplete Si-H site substitution by the mesogenic side chains, and changes in the polydispersity and/or fractionation of the sample during purification. Whatever the cause(s), the effects on $T_{N-I}$ for the $OC_4$ and $OC_6$

homologues are considerable (≈ 10 °C), and in our present state of knowledge, the possibility exists that the effects have been caused by the influence of the backbone on the anisotropic alignment (order parameter) of mesogenic side chains with particular lengths of alkoxy terminal group. These points collectively illustrate that transition temperatures for SCLCP are affected by many more factors than their low molar mass analogues, many being unique to macromolecular systems and often difficult to control.

***Figure 4.14***

*'Odd-even' alternation effect for a series of laterally attached SCLCP bearing terminal alkoxy groups*

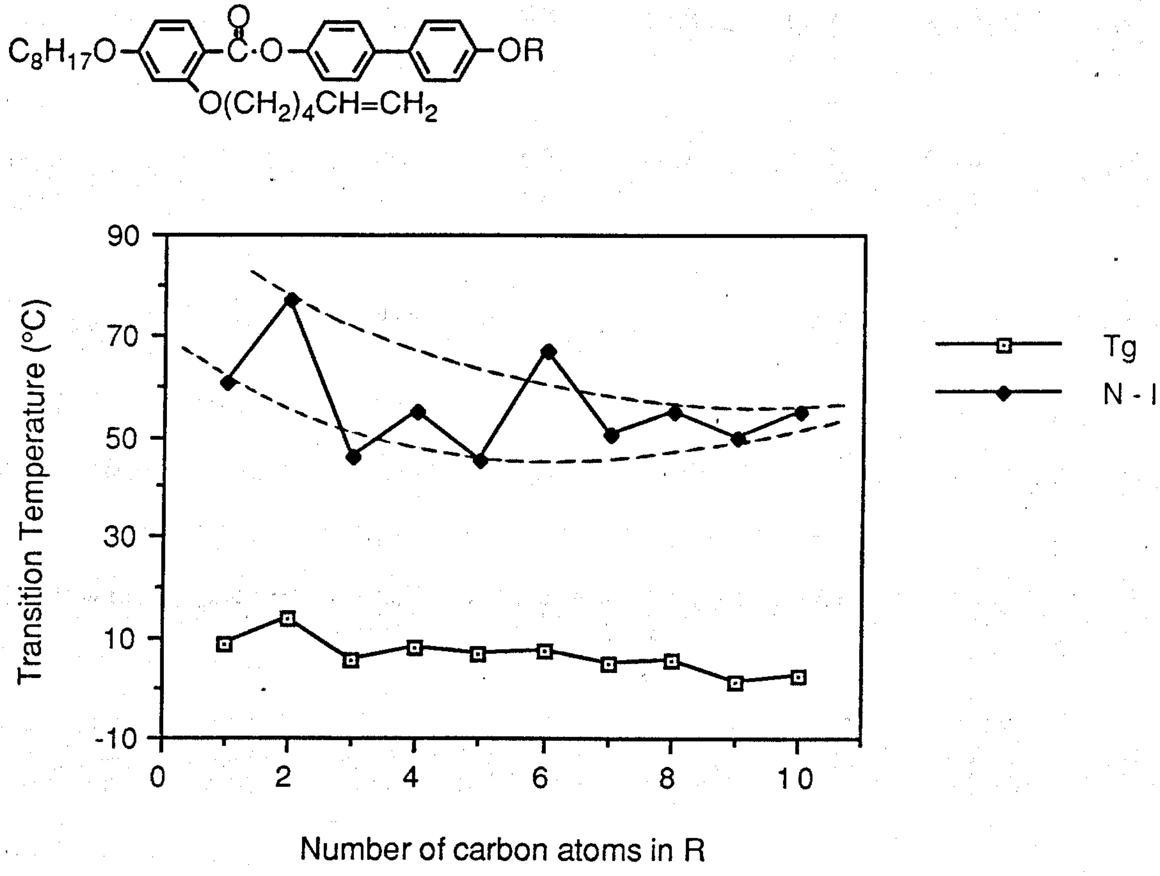


*Table 4.13*

*Phase transition temperatures and enthalpies of clearing for a homologous series of laterally attached side chain polysiloxanes bearing terminal alkoxy groups*

| | | Tg t/°C | | N - I t/°C | | ΔH cal/g |
|---|---|---|---|---|---|---|
| | | ONSET | MID-PT | ONSET | MAX | |
| W38 | **5e** | 6.7 | 8.7 | 58.3 | 60.6 | 0.12 |
| W39 | **5f** | 13.2 | 14.0 | 72.3 | 77.0 | 0.24 |
| W40 | **5g** | 5.3 | 6.0 | 41.0 | 46.0 | 0.13 |
| W41 | **5h** | 4.3 | 8.3 | 49.8 | 54.8 | 0.17 |
| W42 | **5i** | 4.8 | 7.2 | 41.0 | 45.6 | 0.07 |
| W43 | **5j** | 4.6 | 7.3 | 62.8 | 66.7 | 0.23 |
| W44 | **5k** | 2.4 | 5.2 | 47.5 | 50.4 | 0.12 |
| W45 | **5l** | 3.3 | 6.0 | 51.5 | 54.5 | 0.09 |
| W46 | **5m** | 0.1 | 1.5 | 46.1 | 49.7 | 0.10 |
| W47 | **5n** | 1.5 | 2.5 | 51.9 | 54.6 | 0.15 |

### 4.3.2 End-group Efficiency

The results from these investigations have been largely disappointing (Table 4.14). The low mesophase thermal stabilities of the side chain precursors, a consequence of the long lateral alkenyl chains which disrupt nematic packing, coupled with the unique effect resulting in the reduced transition temperatures exhibited by these novel systems on moving from side chain precursor to polymer, have meant that many of the SCLCP synthesised are non-mesomorphic. As such, this study has been inconclusive in the development of structure-property correlations for SCLCP, but a nematic terminal group thermal stability order based on the isotropisation temperatures of the low molar mass side chain precursors has been constructed.

*Table 4.14*

*Phase transition temperatures and enthalpies of clearing for laterally attached side chain polysiloxanes derived from side chain precursors given in Table 4.1, now appended to this section (Appendix to Section 4.3) for the reader's convenience*

| | | Tg<br>t/°C | | N - I<br>t/°C | | ΔH<br>cal/g |
|---|---|---|---|---|---|---|
| | | ONSET | MID-PT | ONSET | MAX | |
| W48 | **5o** | 6.0 | 8.0 | - | - | - |
| W49 | **5p** | -2.7 | -0.1 | - | - | - |
| W50 | **5q** | 5.0 | 6.0 | - | - | - |
| W51 | **5r** | 2.0 | 5.0 | - | - | - |
| W52 | **5s** | 4.9 | 5.8 | - | - | - |
| W53 | **5t** | 10.8 | 12.8 | - | - | - |
| W54 | **5u** | 9.2 | 10.0 | 46.7 | 47.8 | 0.07 |
| W55 | **5v** | 20.6 | 21.3 | - | - | - |
| W56 | **5w** | 4.3 | 6.7 | - | - | - |
| W57 | **5x** | -3.9 | 0.1 | - | - | - |
| W58 | **5y** | -9.0 | -3.5 | - | - | - |
| W59 | **5z** | 3.7 | 4.7 | - | - | - |
| W60 | **5aa** | 5.9 | 9.2 | - | - | - |
| W61 | **5ab** | 17.8 | 22.0 | - | - | - |
| W62 | **5ac** | 20.0 | 23.0 | - | - | - |
| W63 | **5ad** | 7.3 | 8.4 | 27.3 | 30.9 | 0.12 |
| W64 | **5ae** | 2.0 | 3.3 | 16.6 | 18.7 | 0.11 |
| W65 | **5af** | 14.5 | 16.0 | - | - | - |
| W66 | **5ag** | 17.2 | 19.4 | - | - | - |
| W67 | **5ah** | 22.6 | 24.3 | - | - | - |
| W68 | **5ai** | 10.0 | 10.6 | - | - | - |
| W69 | **5aj** | 10.0 | 10.4 | - | - | - |

The thermal properties of polymers bearing terminal cyano- or pentyl- groups have already been described in earlier sections. Both these end-groups were in side chain precursors having lateral substituents with either five or six carbon atoms, and this provided results relating to changing chain length on the phase transition temperatures of the side chain precursors. In these cases, the odd carbon chain members which constitute the lateral attachment have higher transition temperatures than the even members by 5 - 8 °C (see Appendix to Section 4.3). The value of $T_{N-I}$, however, is seen to decrease for the side chain precursors as the length of the lateral $O(CH_2)_nCH=CH_2$ group is increased, presumedly due to the 'dilution' of the mesophase by the increased separation of the molecules and the reduction in the anisotropy of the intermolecular attractions. The side chain precursor **JSH**, with eleven carbon atoms and a terminal cyano-group, is thus observed to exhibit a clearing temperature much lower than that recorded for its five and six carbon analogues, **5a** and **5b** respectively. Furthermore, the 'parent' compound of the terminal cyano side chain precursor, i.e., with no lateral alkenyloxy group, has been reported to have a clearing temperature of 240 °C. This material gives nematic and smectic A phases and exhibits reentrant nematic behaviour [41]. The introduction of the lateral group which constitutes the spacer attachment in the SCLCP has thus reduced $T_{N-I}$ by *ca.* 180 °C, as well as having suppressed smectogenic properties.

The properties of the homologous series with terminal alkoxy groups have already been discussed in the preceding section. Terminal substitutions of this unsymmetric kind could be achieved easily for these side chain precursors, allowing for the creation of a chiral environment in the mesogenic group by the introduction of suitable branched chain substituents as the terminal group X. The chiral 2-methylbutyl group in the alkene is known to show a monotropic cholesteric-isotropic transition at 30 °C [42]. In order to increase the clearing point, the same chiral unit was used, but in this case as a terminal alkoxy group, to obtain the derivative **5o**, which gave a Ch - I transition of 42.8 °C. The effect of the oxygen in the alkoxy system has therefore raised the chiral nematic thermal stability by *ca.* 13 °C relative to the alkyl analogue. This increment is consistent with that observed for another pair of preparations -- see side chain precursors **5c** and **5i**, where a change in the end-group from pentyl to pentyloxy has increased the N - I transition temperature by 15 °C. However, such a chiral nematic thermal stability was not sufficiently high for the corresponding polymer to exhibit liquid crystallinity (see W48 in Table 4.14). Another two chiral terminal groups were also used, X = $OCH(CH_3)C_6H_{13}$ (**5p**) and X = $OCH(CH_3)COOC_2H_5$ (**5q**). In both cases, the broadening effect of chain branching at the carbon next to the oxygen reduces the mesophase thermal stability greatly and very low isotropisation temperatures are observed (Appendix to Section 4.3).

The next effect studied was the incorporation of ester groups with different environments in the terminal group X. When located directly onto the ring, side chain precursor **5r** is found to melt at a fairly high temperature. The onset of rapid crystallisation, on cooling the sample, made detection of any precise nematic-isotropic transition difficult, although it was estimated to occur at about 70 °C. The introduction of a methylene unit between the ester function and the benzene ring (**5s**) has the effect of aligning the $COOCH_3$ group off-axis and reducing the anisotropy of molecular polarisability, and this is reflected in the dramatic fall in nematic thermal stability to below 19.8 °C. Introduction of the second methylene group in **5t** brings the $COOCH_3$ group more back into line, and the $T_{N-I}$ rises to 29.8 °C. However, when the conjugation of the system is enhanced, by having an unsaturated alkenic link between the ester group and the ring, the side chain precursor **5u** has a much higher clearing temperature of 122.5 °C; incidentally this is the only side chain precursor of this type to have an isotropisation temperature above 100 °C. As found before, chain branching significantly reduces the mesophase thermal stability, as shown by **5v**, with X = $CH(CH_3)CH_2COOCH_3$, being non-mesomorphic, and **5w**, a branched analogue of **5r**, having a low $T_{N-I}$.

As mentioned earlier, when the terminal group X is a chiral 2-methylbutyl group, the side chain precursor has a clearing temperature of 30 °C. The chiral 3-methylpentyl (**5x**) and 4-methylhexyl (**5y**) homologues were prepared, with the intention of obtaining cholesteric polymeric phases with different pitch senses and pitch lengths if the laterally attached SCLCP exhibited cholesteric phases. In the event, the polymers were not liquid crystalline (W57 and W58). Considering the side chain precursors, depressions in $T_{N-I}$ are known to be smaller when the chiral centre in the branched substituent is moved further away from the core by attaching it to flexible parts of the terminal chain [43]. This allows the substituent to be more readily accommodated in the normal rotational volume of the alkyl chain. In these cases, the temperatures recorded (**5w, x, y** in Appendix to Section 4.3) are largely similar.

A biphenylyl group without a substituent at the *para-* position (see **5z**, X = H) failed to give a mesomorphic side chain precursor. This was anticipated, since the terminal H is unable to enhance the anisotropy of molecular polarisability [44].

A few side chain precursors with terminal halogen substituents were also synthesised -- precursor **5ac**, with a polarisable Br gave a nematic-isotropic transition at 49 °C, while the fluoro-analogue **5aa** cleared at a considerably lower temperature. The trifluoromethyl derivative **5ab** was also prepared for comparison with the fluoro-compound, and was found to give a more thermally stable nematic phase.

In summary, on the basis of the thermal data collected from these side chains precursors, a nematic terminal group efficiency order in X may be constructed and is

$CN > Alkoxy > Alkyl > Br > CF_3 > F > H$

It is interesting to note that this is in accord with empirical rules established for the effect of terminal substituents on nematic thermal stability for several other series of low molar mass materials [44]. Apparently therefore, the lateral ω-alkenyloxy groups in the side chain precursors do not cause deviations from the rules established for simpler series of mesogens. The side chain precursors corresponding to the first three members of the above order, i.e., CN, alkoxy and alkyl, were the only ones to give rise to liquid crystalline polymers. This might imply that the above nematic thermal stability order will apply to the polymers as well as the side chain precursors. However it is noted in the case of side chain precursor **5u** (X = $CH{=}CHCOOCH_3$), which has the highest nematic-isotropic transition temperature of all the precursors synthesised in this work, that although the polymer W54 also shows a nematic mesophase, its clearing temperature has been dramatically reduced to about that typical for the polymers with terminal alkoxy groups as X.

Finally, it should be stressed that in all of the examples, the trend of falling transition temperatures, on moving from side chain precursors to the polymeric systems, has been observed, except where terminal group X = CN. It is assumed that this is a result of differing extents and effectiveness of pairwise correlations between the polar groups in the precursor and the polymer.

### 4.3.3 Changing The Mesogenic Core

Some modifications to the general mesogenic core were made in order to investigate the effect of structural changes on the characteristics of the system. The third or 'outer-most' phenyl ring in the precursor was replaced by a *trans*-1, 4-cyclohexane ring to give the cyclohexylphenyl benzoate (**5ae**) -- structures for precursors **5ae** to **5aj** are given in the Appendix to Section 4.3. The change in this case reduces the nematic thermal stability by *ca.* 10 °C, in comparison to the biphenylyl analogue **5ad**. This difference in clearing temperatures is maintained between the polymeric versions (W63 and W64, Table 4.14). Though observed before [45], this decrease is an inversion of the nematic thermal stability order found for many pairs of nematic biphenyl and cyclohexylphenyl derivatives. It is normally advantageous to a system therefore to incorporate a fairly flexible cyclohexane ring in place of a phenyl ring, since it appears to permit better nematic packing. However, the attachment of such an entity to the rigid extended core is found to be detrimental to the nematic ordering in the cases of the side chain precursors and the SCLCP under discussion.

The biphenyl unit of the terminal cyano side chain precursor, **5a**, was also replaced by a 2, 6-naphthalene unit (**5af**). As reported by Coates and Gray, this broadens the molecule considerably, thereby reducing the length-breadth ratio, an effect which causes a large fall in clearing temperature [46]. As can be seen in the appendix to this section, the $T_{N\text{-}I}$ of **5af** is below 0 °C, and the corresponding polymer W65 in Table 4.14 is not liquid crystalline.

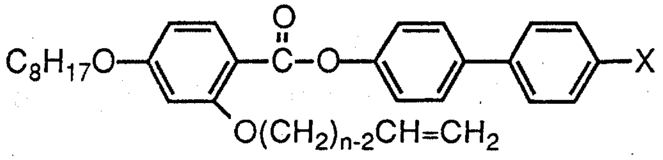
Antiparallel correlations between terminal polar cyano-groups result in higher than expected transition temperatures, but reduce the true potential of the system to give really large positive dielectric anisotropies. One method of decreasing such molecular associations is by the introduction of fluoro-groups *ortho*- to the polar group [47]. The fluoro-substituent is commonly used because it is the smallest substituent possible and so has the least effect in broadening the molecule. Although clearing transition temperatures are suppressed to some extent, the dielectric properties are enhanced because of the reduced antiparallel correlations. As such, the use of one and two fluoro-substitutions *ortho*- to a cyano end-group has been examined for several systems. With two *ortho*- fluoro-substituents, the dipolar contributions to $\varepsilon_\perp$ cancel, and the components along the long axis reinforce to enhance $\varepsilon_{||}$ and make $\Delta\varepsilon$ even more positive. In the case of the side chain precursors of interest in this work, one such lateral substituent gives **5ag** and reduces the nematic clearing temperature by 26.6 °C. A second fluoro-substituent, side chain **5ah**, further depresses the N - I temperature by 41.5 °C. The introduction of the first fluoro-group may for certain rotational conformers broaden the molecule, but this effect can be diminished through rotations about the O-acyl bond. A second fluoro-group, however, inevitably increases the width of the molecule. These effects are reflected in the unequal decreases in clearing temperatures, and are consistent with those previously observed in these laboratories for other low molar mass systems [48]. Unfortunately, the effects of reducing antiparallel correlations, which are expected to be more extensive for the polymeric systems as proposed in Section 4.2.2, could not be confirmed as only amorphous polymers were obtained from these two side chains. This was partly due to the high glass transition temperatures, which prevented the observation of any nematic phases in the polymers (W66 and W67).

The absence of any detectable phase in the polymer derived from side chain **5ag** (Side chain: K 67.5 N (39.8) I. Polymer: Tg 19.4) means that the I - N transition must occur at a temperature below the glass transition (< 19.4 °C). This implied reduction in transition temperature compared to that of the precursor may be interpreted as being due to the absence of any substantial antiparallel correlations.

Lateral fluoro-substituents were also incorporated into the parent terminally bromo-substituted side chain **5ac**. These fluoro-substituents were sited on different rings and in each of the two different positions (A and B) shown in structures **5ai** and **5aj**. By comparing the N - I transition temperatures, both of which are markedly lower than that for the terminal bromo-analogue **5ac** (by 36.8 °C and 28.8 °C for **5ai** and **5aj** respectively) due to the steric twisting about the inter-ring bond, it can be assumed that by having the fluorine in the same ring as the bulky bromo-substituent (**5aj**), the increase in the breadth of the molecule is less than when the fluorine is substituted on the other ring (**5ai**). In other words, the smaller observed decrease in clearing temperature relative to the parent unit occurs for **5aj**. The polymers derived from these side chains were again not liquid crystalline (W68 and W69) and the Tg values were quite high (> 10 °C).

It has been noted that higher glass transition temperatures have been recorded for polymers whose side chains have rigid or bulky groups (**5v**, **5ab**, **5ac**, **5ai**, **5aj**). These 'occupy' a large volume and in order to achieve backbone rotations, considerable energy is required. This consequently elevates glass transition temperatures. The effect of flexible side groups on the free volume of the system, on the other hand, is not as significant, and lower Tg values result (typically *ca.* 7 °C). Where polar groups are present (**5a**, **5b**, **5af**, **5ag**, **5ah**), the inter-side chain attractions effectively reduce the free volume of the system, and increases in Tg are again observed.

## *Appendix to Section 4.3*



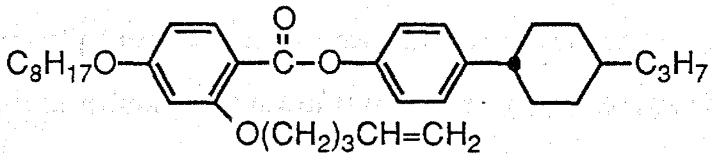
| Cmpd No | n | X | K - N, I | N - I |
|---|---|---|---|---|
| **5a** | 5 | CN | 67.5 | (66.4) |
| **5b** | 6 | CN | 74.5 | (58.2) |
| **5c** | 5 | $C_5H_{11}$ | 44.5 | 50.2 |
| **5d** | 6 | $C_5H_{11}$ | 42.2 | 45.2 |
| **5e** | 6 | $OCH_3$ | 102.2 | (□) |
| **5f** | 6 | $OC_2H_5$ | 98.0 | (77.5) |
| **5g** | 6 | $OC_3H_7$ | 89.2 | (51.4) |
| **5h** | 6 | $OC_4H_9$ | 80.8 | (74.0) |
| **5i** | 6 | $OC_5H_{11}$ | 75.0 | (65.5) |
| **5j** | 6 | $OC_6H_{13}$ | 63.5 | 71.6 |
| **5k** | 6 | $OC_7H_{15}$ | 57.0 | 66.5 |
| **5l** | 6 | $OC_8H_{17}$ | 50.3 | 68.9 |
| **5m** | 6 | $OC_9H_{19}$ | 46.0 | 67.6 |
| **5n** | 6 | $OC_{10}H_{21}$ | 55.0 | 68.9 |
| **5o** | 5 | $OCH_2CH(CH_3)C_2H_5$ | 67.0 | (42.8)* |
| **5p** | 5 | $OCH(CH_3)C_6H_{13}$ | 36.8 | (5.7)* |
| **5q** | 5 | $OCH(CH_3)COOC_2H_5$ | 52.0 | (-5.0)* |

---

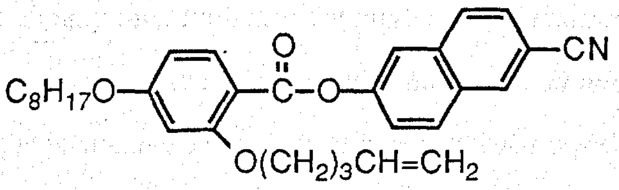
□ Monotropic phase transition temperature difficult to determine due to fast recrystallisation.

* Chiral nematic-isotropic transition.

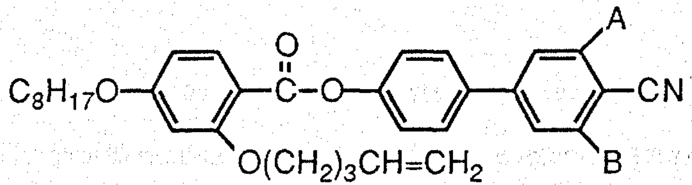
| | | | | |
|---|---|---|---|---|
| **5r** | 5 | $COOCH_3$ | 90.6 | (¤) |
| **5s** | 5 | $CH_2COOCH_3$ | 71.7 | (19.8) |
| **5t** | 5 | $(CH_2)_2COOCH_3$ | 56.0 | (29.8) |
| **5u** | 5 | $CH=CHCOOCH_3$ | 103.5 | 122.5 |
| **5v** | 5 | $CH(CH_3)CH_2COOCH_3$ | 54.5 | - |
| **5w** | 5 | $COOCH_2CH(CH_3)C_2H_5$ | 63.4 | (32.6)* |
| **5x** | 5 | $(CH_2)_2CH(CH_3)C_2H_5$ | 44.4 | (32.6)* |
| **5y** | 5 | $(CH_2)_3CH(CH_3)C_2H_5$ | 41.3 | (32.2)* |
| **5z** | 5 | H | 92.7 | - |
| **5aa** | 5 | F | 68.3 | (30.4) |
| **5ab** | 5 | $CF_3$ | 79.2 | (38.0) |
| **5ac** | 5 | Br | 67.7 | (49.0) |
| **5ad** | 5 | $C_3H_7$ | 57.5 | (50.3) |
| | | | | |
| **JSH** | 11 | CN | 48.2 | (43.4) |



**5ae** : K 56.0 N (41.0) I.

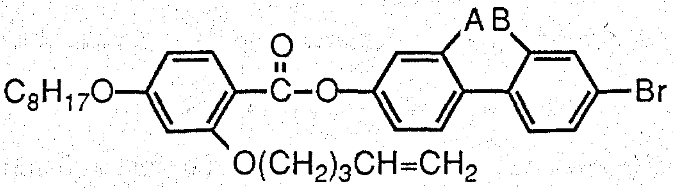


**5af** : K 61.2 N (-1.5) I.



**5ag** : A = F, B = H; K 67.5 N (39.8) I.

**5ah** : A = F, B = F; K 45.3 N (-1.7) I.



**5ai** : A = F, B = H; K 52.7 N (12.2) I.

**5aj** : A = H, B = F; K 64.0 N (20.2) I.

## 4.4 MIXED LATERAL/TERMINAL COPOLYSILOXANES

In view of the demand for liquid crystal polymers which exhibit specific thermal and physical properties, there is a need for relevant parameters to be pre-determined, and this is possible through the use of appropriate mesogenic appendages to a suitable polymer backbone. For even greater scope, this may also be achieved by the synthesis of side chain copolymers containing two or more mesogenic moieties, since variation of type and ratio of side chain allows for the fine tuning of polymer characteristics. This technique has already been applied in the production of practically useful polysiloxanes [4], in an analogous manner to the making of LMM binary mixtures. By extending this principle, it was considered a viable project to synthesise novel siloxane copolymers containing varying amounts of both terminally and laterally attached mesogenic groups, since this might offer a further degree of control over the physical parameters of the resultant SCLCP [49].

Preliminary studies of these new systems involved the synthesis of copolymers with a 50:50 mol-% ratio of side chains, where the lateral precursor (**5b**) had a terminal cyano component and the conventionally attached side chain (**7d, 7e**) terminated in either an alkyl or an alkoxy group (Table 4.15, Figures 4.15 and 4.16).

All literature reports on laterally attached polysiloxanes to date show these polymers to be nematic and although both terminally attached homopolymers exhibit additional smectic properties, stable over a fairly wide thermal range in the case of the terminal methoxy terminally attached homopolymer, the two copolymers from Series A and B are purely nematic in character. From the graphs (Figures 4.15 and 4.16), a similar trend is observed to that involving the study of polar/non-polar, laterally attached side chain copolymers (Figure 4.1), and the deviation from linearity in N - I transition temperatures may once again be interpreted as due to the break up of polar group antiparallel side chain correlations by the terminally attached side chains bearing alkyl or alkoxy end-groups.

*Table 4.15*

*Phase transition temperatures and enthalpies of clearing for mixed laterally/terminally attached copolysiloxanes, Series A (**5b** and **7d**) and Series B (**5b** and **7e**) and for related side chain homopolymers*

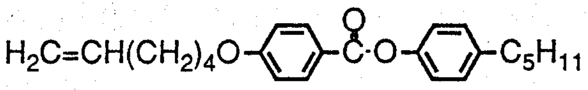
| | Alkenes mol-% | | | | Tg t/°C | S - N t/°C | N - I t/°C |
|---|---|---|---|---|---|---|---|
| W9 | **5b** | 100 | **7d/e** | 0 | 25.1 | - | 82.1 |
| W70 | **5b** | 50 | **7d** | 50 | 6.0 | - | 64.0 |
| W71 | **5b** | 0 | **7d** | 100 | -5.4 | 66.5 [C] | 79.0 |
| W72 | **5b** | 50 | **7e** | 50 | 10.3 | - | 60.5 |
| W73 | **5b** | 0 | **7e** | 100 | 5.0 | 36.0 [A] | 104.0 |

A : Smectic A-isotropic transition.
C : Smectic C-isotropic transition.

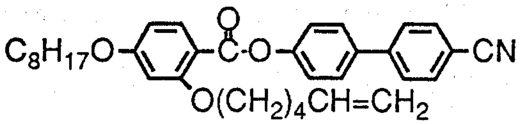
On the basis of these results, this type of copolymer was considered worthy of further investigation and several interesting systems were selected for extensive study (see Sections 4.4.2 - 4.4.5). Gray, Hill and Lacey were the first to report the synthesis of such novel copolymers [50], derived from a series in which the terminally attached homopolymer (terminal cyano) has a relatively high melting and clearing point, and the laterally attached homopolymer (terminal nonyloxy) is nematic with a glass transition. The main feature of this copolymer system is that the introduction of only small amounts of lateral side chain component into a predominantly terminally attached system has extremely striking repercussions, as opposed to the converse situation where the effect is very small. The presence of lateral side chains above a certain low concentration first introduces a narrow thermal range nematic phase above the $S_A$ phase; the smectic properties are then quickly extinguished at slightly higher concentrations and a purely nematic polymer system is obtained, and maintained with very roughly constant $T_{N-I}$ values right across the diagram of state to the homopolymer with 100% of laterally attached side chains.

***Figure 4.15***

*Phase transition temperatures relating to a mixed lateral/terminal copolysiloxane, Series A, bearing lateral side chain **5b** and terminal side chain **7d***



**7d**



**5b**

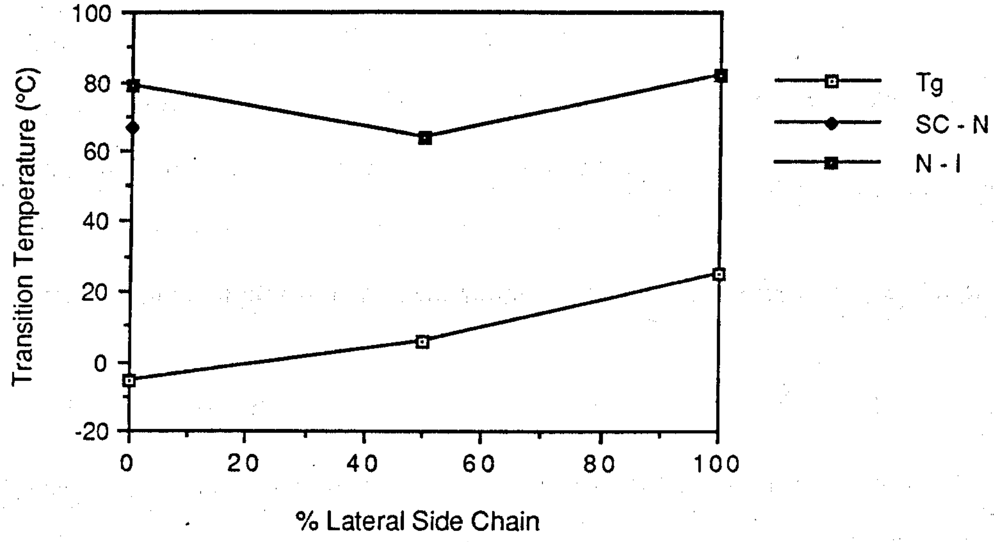
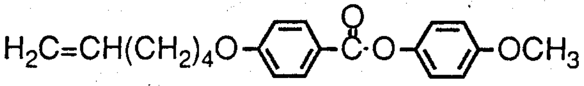
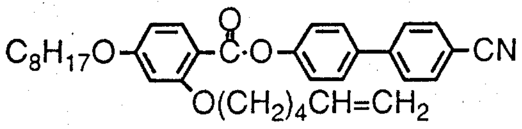


***Figure 4.16***

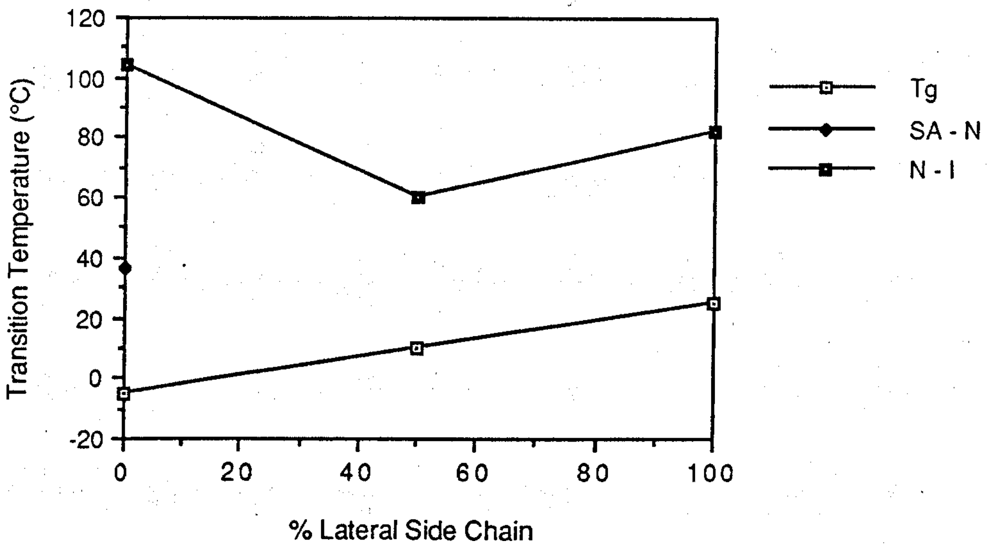
*Phase transition temperatures relating to a mixed lateral/terminal copolysiloxane, Series B, bearing lateral side chain **5b** and terminal side chain **7e***



**7e**



**5b**



Besides providing an avenue for obtaining control over the thermal and physical attributes, it has been found that these mixed copolymer systems align much better in an electric field [51]. This is important, because a big problem surrounding the study and applications of SCLCP is that of obtaining good sample alignment; this has certainly been the case with many terminally attached species. Laterally attached SCLCP, on the other hand, have generally been found to align with greater ease, but tend to lose this alignment after the field has been removed. With the advent of these lateral/terminal copolysiloxanes, the advantages from both systems appear to have been nicely incorporated, since polymer alignment can be achieved easily, and the alignment is maintained on removal of the field. Furthermore, the copolysiloxanes can be switched to either a homeotropic or a planar alignment simply by changing the frequency of the a.c. voltage.

In Section 4.2.6, a comparison of side chain ratios, between reaction feed-stock and ratio actually achieved, was discussed. For those examples, the deviations were found to be small. However, the situation for the copolymers now under discussion is complicated by the vastly different natures of the side chain precursors. The terminal:lateral ratio in each copolymer had to be individually determined by $^1$H NMR, and this was always found to be greater compared to the ratio initially used in the reaction feed-stock. This implies that the rate of hydrosilylation is greater for the terminal than for the lateral alkene, and this is readily understood in terms of the greater steric hindrance to the approach of the lateral moiety to the reaction site.

### 4.4.1 A Proposed Model For Lateral/Terminal Side Chain Copolymers

Zhou *et al.* have suggested that laterally attached SCLCP adopt a 'mesogen-jacketed' type of structure [7], as depicted in Figure 4.17a. Some evidence for this arrangement has been obtained from x-ray diffraction patterns of drawn fibres of laterally attached polyacrylates, where the side groups are observed to align parallel to the draw direction [52]. This implies that the mesogenic groups adopt an arrangement wherein they lie parallel to the polymer backbone. If this is the case, the nematic phase of a laterally attached SCLCP may be considered as analogous to the prolate $N_{III}$ model proposed by Wang and Warner for the nematic phase of a terminally attached SCLCP (Figure 4.17d) [19].

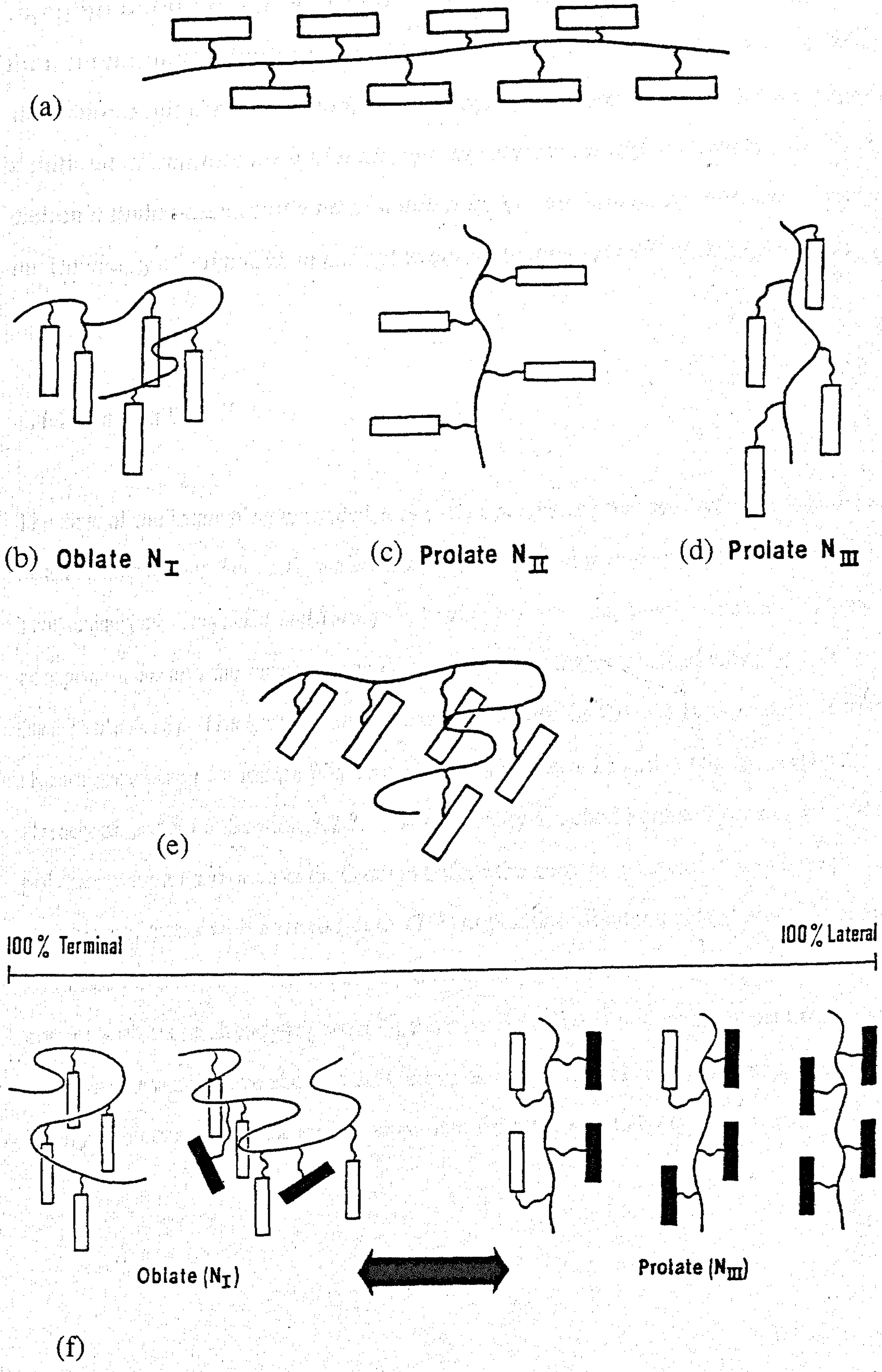
For the prolate model of the nematic phase, the polymer backbone is stretched out by the aligning forces to give a rod-like configuration. The backbone with this arrangement would be expected to have lost more entropy than it would in the oblate $N_I$ model (Figure 4.17b), and to contribute significantly by a corresponding increase in the free energy of the system. This rise in energy would then affect the nematic ordering of the side chains, giving a consequential reduced thermal stability of the phase, reflected in a low observed N - I transition temperature [42]. These arguments may explain why the laterally attached SCLCP reported show only modest increments in their isotropisation temperatures on moving from monomer to polymer [23], and not the larger temperature increases and/or phase stabilisations that constitute the 'polymer effect', a feature commonly associated with terminally attached SCLCP [5]. The manner in which the mesogenic groups are arranged around the polymer backbone probably also explains the distinctive lack of smectic properties in laterally attached SCLCP, despite the use of long terminal alkyl groups and/or terminal polar groups and 6 and 7 atom spacers.

Turning specifically now to the novel lateral side chain precursors prepared in the current work, these have the point of attachment of the side chain located on the first ring of the three-ringed system. This gives it an off-centred and unbalanced effect, so that the side chains may possibly be positioned not parallel, but tilted at an angle to the polymer backbone (Figure 4.17e). This behaviour of the side chains as 'quasi-terminal' units may, based on mechanical arguments, result in greater coupling between the motions of side chains and the main chain, compared with the polymers described by Keller *et al.* [53], where the spacer connection is closer to the centre of the mesogenic core. This factor may be responsible for the reduced N - I transition temperatures observed exclusively for these systems on passing from monomer to polymer, and not consistent with the small increases reported in the literature for nearly all of the rather small number of other known laterally attached SCLCP [6, 7].

The Wang and Warner models may also be used to explain the arrangement adopted by the side chains in the mixed copolysiloxanes which have both laterally and terminally attached mesogenic groups appended along the polymer backbone [42]. In the laterally attached homopolymer, the backbone and mesogenic groups may take up the prolate $N_{III}$ arrangement as already discussed. With the introduction of terminally attached mesogenic groups, these side chains may be accommodated in a similar type of prolate arrangement without disrupting the nematic ordering. The transition temperatures have indeed been observed to remain reasonably constant for up to a 70% terminal side chain population [50]. Conversely, the polymer backbone is likely to tend towards an oblate $N_I$ arrangement for the smectic phase of a terminally attached homopolymer. This is because in the smectic phase, the mesogenic side chains must lie in layers, and the backbone is drawn into the planes between the layers, as a result of the linkage between polymer and side chains. As laterally attached mesogenic groups are added here, the outcome may be for the side chains to behave initially as quasi-terminals (Figure 4.17e), which significantly disrupt the smectic ordering. This leads to the large observed decreases in smectic-nematic transition temperatures. Eventually, as more lateral mesogenic groups are attached, these side chains probably promote a gradual alteration in backbone orientation from the oblate $N_I$ to the prolate $N_{III}$, consistent with the change in phase type from smectic to nematic. The above sequence of events is shown in Figure 4.17f.

*Figure 4.17*

*Possible configurations for laterally attached, terminally attached and mixed lateral/terminal copolysiloxanes*



This hypothesis is to some extent substantiated by dielectric studies carried out on these copolymer systems, where a change in sign of the dielectric anisotropy ($\Delta\varepsilon$) from negative to positive occurs as the temperature is increased [42]. This suggests that the copolymer adopts a prolate $N_{III}$ arrangement at low temperature, which then converts to the more entropically favoured oblate $N_I$ arrangement as the temperature is increased, since the entropic contribution to the free energy of the system is more likely to have a significant influence on the spatial arrangement assumed at higher temperatures. Further dielectric studies are currently being undertaken, in addition to x-ray diffraction studies at the University of Bristol, in an attempt to elucidate the structures of these polymers.

### 4.4.2 Series C

The first of the interesting extended series of copolymers prepared (referred to at the start of this section) was Series C, which involved a reversal in end-groups from that synthesised by Gray, Hill and Lacey [50], having the terminal cyano sited on the lateral component **5b** and the terminal nonyloxy on the terminally attached side chain **7f** (see Table 4.16). The graph obtained from the results in Table 4.16 is analogous to that shown previously (compare Figure 4.18 with Figures 4.15 and 4.16), for reasons already discussed in Section 4.2.2. The terminally attached homopolymer is a crystalline polymer with a narrow smectic C range before the nematic phase; this $S_C$ phase persists in the copolymers with a small (up to 17%) population of lateral side chains, although the nature of the polymer itself has changed from being crystalline to glassy. These results concur with those already reported [50]; the smectic phase is noticeably absent from the copolymers which have above a 20% composition of lateral side chain, supporting the theory of a change in backbone arrangement from the oblate $N_I$ to the prolate $N_{III}$ form.

*Table 4.16*

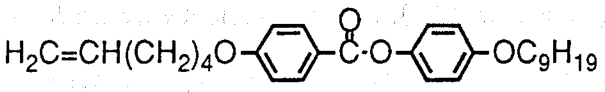
*Phase transition temperatures and enthalpies of clearing for mixed laterally/terminally attached copolysiloxanes, Series C (**5b** and 7f)*

| | Alkenes mol-% | | | | Tg t/°C | $S_C$ - N t/°C | N - I t/°C |
|---|---|---|---|---|---|---|---|
| W9 | **5b** | 100 | **7f** | 0 | 25.1 | - | 82.1 |
| W74 | **5b** | 42.5 | **7f** | 57.5 | 8.2 | - | 64.7 |
| W75 | **5b** | 31 | **7f** | 69 | 10.0 | - | 78.0 |
| W76 | **5b** | 17 | **7f** | 83 | 35.0 | 82.7 | 91.5 |
| W77 | **5b** | 11.2 | **7f** | 88.8 | 37.3 | 88.9 | 95.0 |
| W78 | **5b** | 10 | **7f** | 90 | 38.0 | 91.0 | 96.3 |
| W79 | **5b** | 3.2 | **7f** | 96.8 | 42.6 | 94.1 | 104.2 |
| W80 | **5b** | 0 | **7f** | 100 | 65.0 $^K$ | 95.0 | 104.5 |

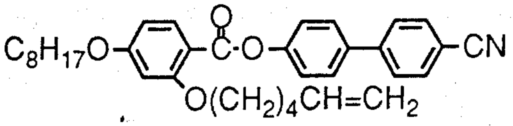
K : Crystal-smectic C transition.

*Figure 4.18*

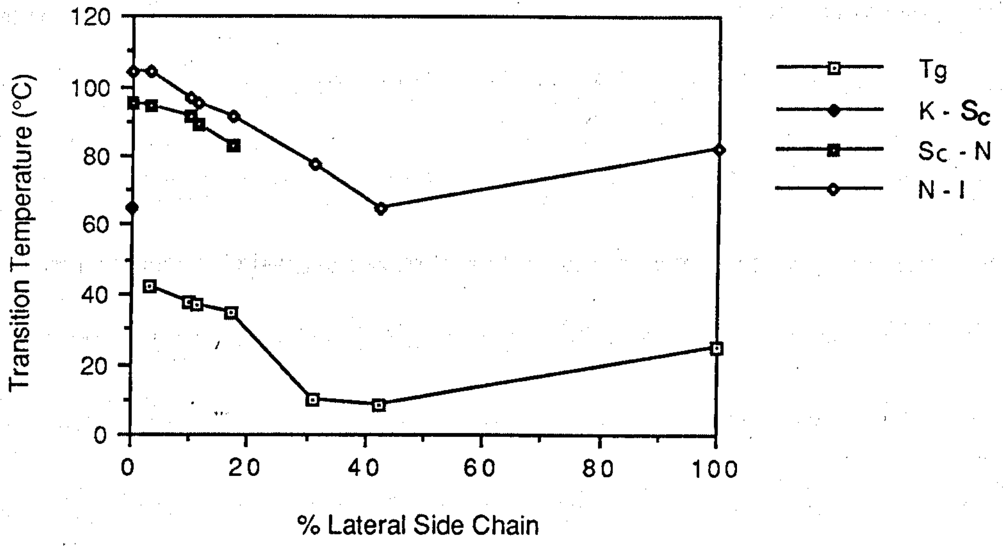
*Phase transition temperatures for mixed lateral/terminal copolysiloxanes, Series C, bearing lateral side chain **5b** and terminal side chain 7f*



**7f**



**5b**



### 4.4.3 Series D

This series was considered interesting to study with regard to the dielectric properties, since both the lateral (**5b**) and terminal (**7c**) side chains in the copolymers carry terminal cyano end-groups. Moreover, it can be seen that both small (> 0%) and large (up to 70%) amounts of terminally attached mesogenic groups can be used without significantly affecting the thermal properties of the laterally attached homopolymer (Figure 4.19 and Table 4.17). This can be advantageous, especially when the terminal side chains contain cyano-groups, since changes in the dielectric properties may then be studied while maintaining other parameters fairly constant [42].

Other points to note in relation to Series C are that, apart from minor fluctuations, the glass transition temperatures vary only slightly across the entire composition range (Figure 4.19). The phase transition temperatures, however, are affected much more dramatically on starting from the left of Figure 4.19. It was difficult to detect the smectic A phase, which the terminally attached homopolymer exhibits with high thermal stability, after adding 6% of lateral side chain component. This may be due to the reductions in the layer promoting antiparallel correlations between the polar groups of the terminal side chains by the lateral side chains. Although the lateral side chains also possess terminal cyano end-groups, these associations may be difficult to constitute. However, the system is difficult to discuss due to the high concentration of cyano-groups in two different environments, and, since no true minimum is observed in the $T_{N\text{-}I}$ line in Figure 4.19, this suggests that antiparallel correlations are still actively present throughout this copolymer system. This mixed system is more sensitive to the amount of lateral side chain included, since very small concentrations (> 6%) of these mesogenic groups are sufficient to suppress the smectic properties, giving the preferred nematic phases with high thermal stabilities.

**Table 4.17**

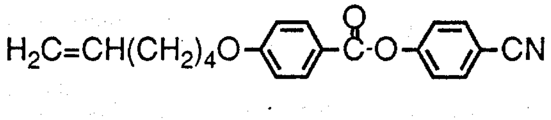
*Phase transition temperatures and enthalpies of clearing for mixed laterally/terminally attached copolysiloxanes, Series D (**5b** and **7b**)*

| | Alkenes mol-% | | | | Tg t/°C | $S_A$ - N, I t/°C | N - I t/°C |
|---|---|---|---|---|---|---|---|
| W9 | **5b** | 100 | **7b** | 0 | 25.1 | - | 82.1 |
| W81 | **5b** | 47.5 | **7b** | 52.5 | 10.6 | - | 76.8 |
| W82 | **5b** | 18 | **7b** | 82 | 10.0 | - | 111.1 |
| W83 | **5b** | 12.2 | **7b** | 87.8 | 6.4 | - | 115.3 |
| W84 | **5b** | 7 | **7b** | 93 | 6.8 | - | 128.3 |
| W85 | **5b** | 5.5 | **7b** | 94.5 | 5.0 | 125.8 | 131.3 |
| W23 | **5b** | 0 | **7b** | 100 | 45.4[K] | 170.0 | - |

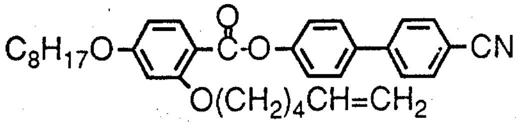
K : Crystal-smectic A transition.

**Figure 4.19**

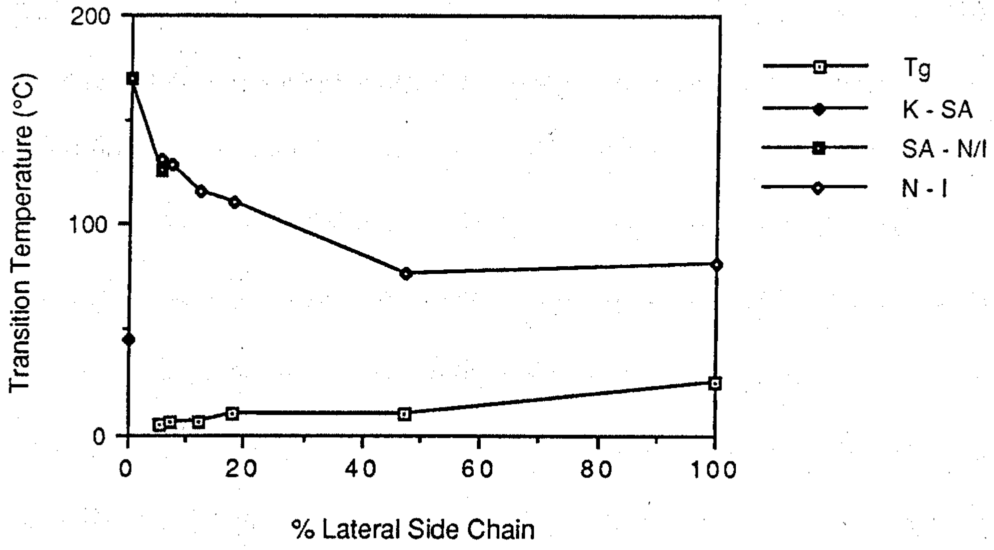
*Phase transition temperatures for mixed lateral/terminal copolysiloxanes, Series D, bearing lateral side chain **5b** and terminal side chain **7b***



**7b**



**5b**



### 4.4.4 Series E

This series was synthesised to examine the effect of chirality on the liquid crystalline properties of these mixed systems; the series was made by the introduction of lateral side chains with terminal cyano-groups (**5b**) into a terminal side chain polymer, where the mesogenic group (**7c**) had end-group chiral 3-methylpentyl -- Table 4.18 and Figure 4.20.

The terminally attached homopolymer is purely smectic, identified from optical studies as having the textural characteristics of $S_C$*. On lateral side chain addition, the nematic phase is quickly (< 8.5%) observed at a temperature above the transition from the chiral smectic C phase. This phase is of course a chiral nematic phase. Although the copolymers investigated in this series did not exceed an 18% population of lateral side chains, the arguments used in previous examples would be expected to be applicable. Therefore at higher concentrations of lateral side chain (> 30%), and since the laterally appended homopolymer is purely nematic, the copolymers should exhibit only the chiral nematic phase.

The fairly high $T_{N-I}$ of the lateral homopolymer and the trend of the $T_{Ch-I}$ line in Figure 4.20 suggests that a fairly pronounced minimum in the clearing point must occur in this series and this may be interpreted in terms of breakdown in antiparallel correlations (see Section 4.2.2).

*Table 4.18*

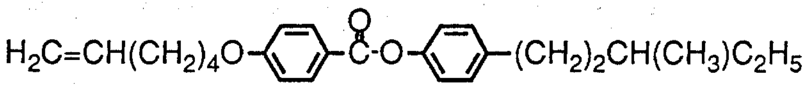
*Phase transition temperatures and enthalpies of clearing for mixed laterally/terminally attached copolysiloxanes, Series E (**5b** and **7c**)*

| | Alkenes mol-% | | | | Tg t/°C | $S_C$* - Ch, I t/°C | Ch - I t/°C |
|---|---|---|---|---|---|---|---|
| W9 | **5b** | 100 | **7c** | 0 | 25.1 | - | 82.1 N |
| W86 | **5b** | 17.5 | **7c** | 82.5 | -2.4 | 22.6 | 33.0 |
| W87 | **5b** | 16 | **7c** | 84 | -2.7 | 24.3 | 34.0 |
| W88 | **5b** | 8.5 | **7c** | 91.5 | -8.5 | 33.3 | 41.3 |
| W89 | **5b** | 0 | **7c** | 100 | -5.0 | 43.2 | - |

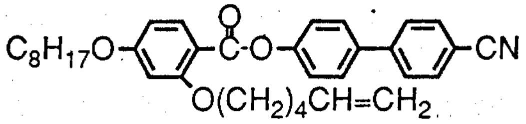
N : Nematic-isotropic transition.

***Figure 4.20***

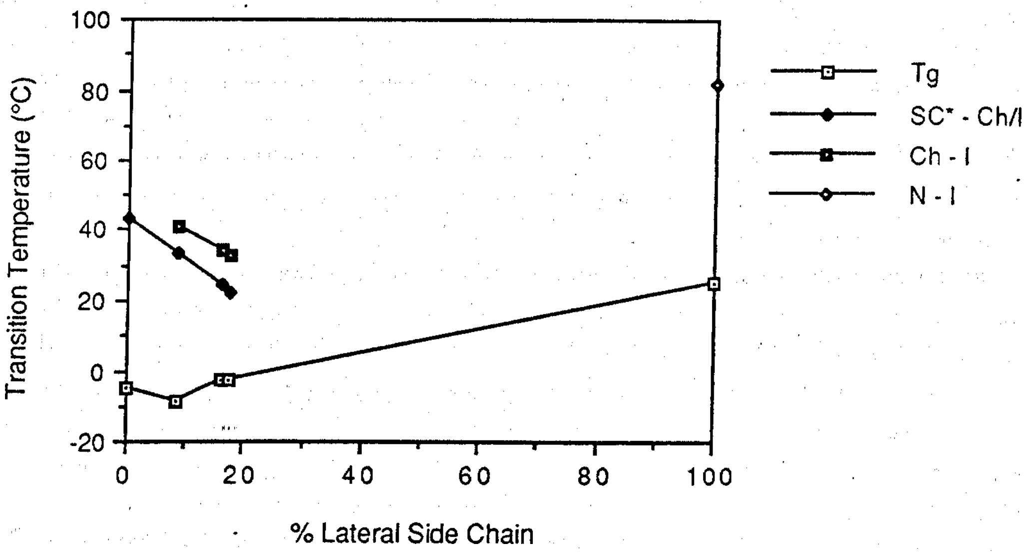
*Phase transition temperatures for mixed lateral/terminal copolysiloxanes, Series E, bearing lateral side chain **5b** and terminal side chain **7c***



**7c**



**5b**



### 4.4.5 Series F

In this series, the chiral unit (X = $COOCH_2CH(CH_3)C_2H_5$) was now present as a terminal group in the lateral side chain (**5w**), while the terminal polar group (X = CN) was on the terminally attached mesogenic group (**7a**). The lateral side chain precursor **5w** shows a monotropic chiral nematic to isotropic transition at 32.6 °C. With this low phase transition temperature (a consequence of chain branching), it is not surprising that the lateral homopolymer W56 is not mesomorphic. As in Series D, the terminally attached homopolymer has a high melting and isotropisation temperature, and is smectic A in character. Small amounts of lateral side chain were sufficient however to depress the transition temperatures markedly, giving a low Tg and inducing an additional chiral nematic phase (Table 4.19 and Figure 4.21). The $S_A$ - N* phase transition had fallen away rapidly by a lateral side chain content of 8.5%, and was again difficult to detect in materials which had larger proportions of lateral side chains.

Although the laterally attached homopolymer is non-liquid crystalline, the chiral nematic phase is still observed in the copolymers synthesised with up to 25% of lateral side chain concentration. As such, the synthesis of additional preparations, with higher percentages of lateral side chains, should allow a more exact extrapolation of the $T_{Ch-I}$ and Tg transition lines across to the right hand axis. This would give a better estimated value for the chiral nematic to isotropic transition temperature of the laterally attached homopolymer. As shown by the rough extrapolation in Figure 4.21, and with no attempt to introduce a minimum in the clearing point curve, $T_{Ch-I}$ for the lateral homopolymer could be any where from -20 °C to +40 °C. Since no phase is however seen, this transition must be below Tg for polymer W56, i.e., < 6.7 °C. The $T_{Ch-I}$ value may therefore be in the range +6.7 °C to -20 °C.

Therefore although only four copolymers were made in this series, their general behaviour is in accord with those of the more extended series of copolymers discussed in earlier sections.

***Table 4.19***

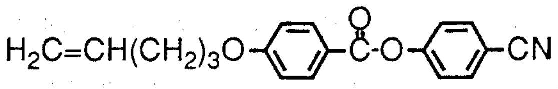
*Phase transition temperatures and enthalpies of clearing for mixed laterally/terminally attached copolysiloxanes, Series F (5w and 7a)*

| | Alkenes mol-% | | | | Tg t/°C | $S_A$ - Ch, I t/°C | Ch - I t/°C |
|---|---|---|---|---|---|---|---|
| W56 | 5w | 100 | 7a | 0 | 6.7 | - | - |
| W90 | 5w | 25.5 | 7a | 74.5 | 9.0 | - | 88.4 |
| W91 | 5w | 15.7 | 7a | 84.3 | 3.4 | - | 105.8 |
| W92 | 5w | 11.5 | 7a | 88.5 | 7.0 | - | 112.7 |
| W93 | 5w | 8.5 | 7a | 91.5 | 9.5 | 61.1 | 126.8 |
| W94 | 5w | 0 | 7a | 100 | 105.4 K | 192.7 | - |

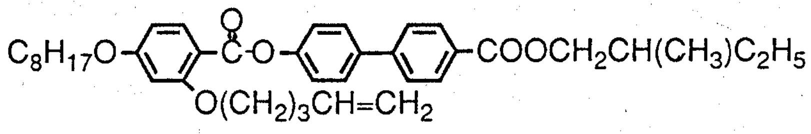
K : Crystal-smectic A transition.

***Figure 4.21***

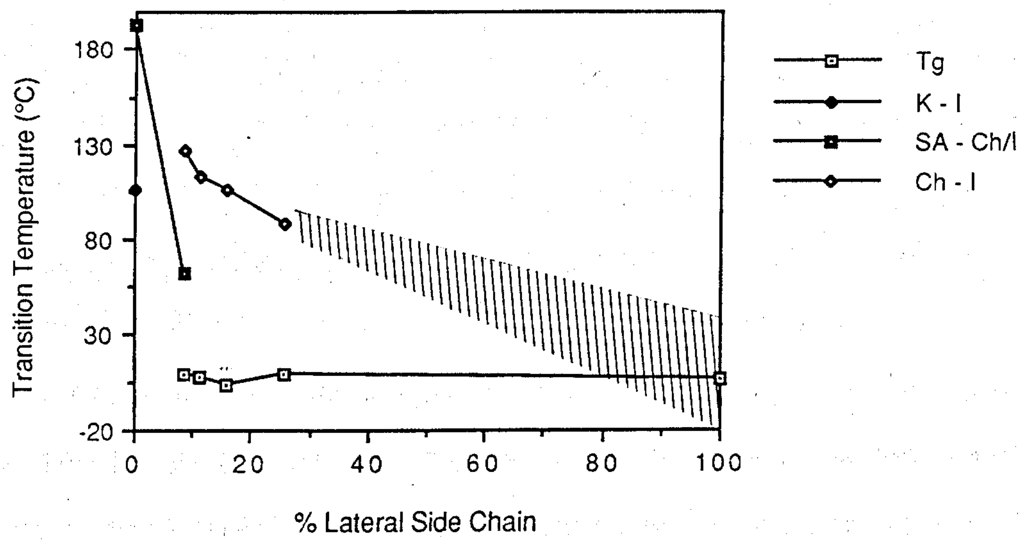
*Phase transition temperatures for mixed lateral/terminal copolysiloxanes, Series F, bearing lateral side chain 5w and terminal side chain 7a*



**7a**



**5w**



## 4.5 TERMINALLY ATTACHED SCLCP WITH LONG LATERAL ALIPHATIC SUBSTITUENTS

Work was diversified to include the synthesis of terminally attached SCLCP with mesogenic groups which carried a lateral substituent of increasing length that was envisaged to lie along the long axis of the side group. The novel vinylic precursors were made (Table 4.5 -- reincluded as an appendix at the end of this section for convenience) and attached to a backbone copolymer polysiloxane. Attempts to append these side groups on a poly(hydrogenmethylsiloxane) homopolymer backbone resulted in the precipitation of the polymer from solution during hydrosilylation, possibly because of severe steric crowding by the bulky side chain precursors.

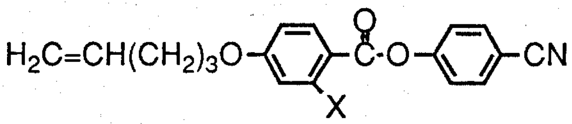
The terminally attached SCLCP were prepared to test the postulate that the long alkyl groups would hinder pairwise correlations of the terminal cyano-groups, thereby enhancing dielectric properties. Weissflog and Demus were the first to report this concept when at that time, the use of such large lateral substituents in LMM systems seemed strongly to contradict the classical rule relating rod-like molecules to liquid crystalline phases [54]. They found that substitution using short alkyl groups ($CH_3$, $C_2H_5$ etc.) brings about dramatic decreases in clearing points, but that the effect then becomes less pronounced with increasing length of the alkyl group, to a point where a more or less constant temperature is reached. Their results suggest that the substituent group first extends outwards in the lateral direction of the molecule and increases the molecular breadth of the mesogenic unit. However, when of sufficient length, the lateral chain is able to distort itself to lie parallel to the molecular long axis, so minimising the molecular breadth effect and producing a molecule of elongated shape.

Takenaka *et al.* have been able to associate this molecular situation with the ability of the long lateral chains to render correlations between terminal polar groups difficult by demonstrating a related increase in dielectric anisotropy [55]. The alteration of the monomer-dimer equilibrium which exists for many terminal cyano-compounds, through the introduction of long substituents in the lateral position, also depresses both the melting point and the mesophase thermal stability. However, these diminished properties have been shown clearly to signal an advantageous increase in the dielectric anisotropy for LMM systems [47].

Turning now to the polymers prepared in the present study, in the case of those with the cyanophenyl ester side chains, the presence of the lateral chain completely extinguishes the mesomorphic properties; only glass transitions are recorded for R = $OCH_3$ to $OC_4H_9$ homologues as they form the isotropic liquid (Table 4.20). Despite the fairly high thermal stability of the unsubstituted parent polymer (P95), which has a $S_A$ - I transition at 98 °C, there were no indications of birefringence when these polymers were examined microscopically above Tg. It was then thought that the lateral substituent might be too short actually to lie along the long axis of the side group, and was in fact protruding outwards. The associated steric effect would explain the absence of liquid crystalline properties. A side chain precursor with an octyloxy group attached laterally was therefore synthesised, but this polymer (P100) was amorphous as well.

***Table 4.20***

*Phase transition temperatures and enthalpies of clearing for terminally attached SCLCP with long lateral aliphatic substituents derived from side chain precursors given in Appendix to Section 4.5*



| | | Tg t/°C | | Tm t/°C | | $S_A$ - I t/°C | |
|---|---|---|---|---|---|---|---|
| | | ONSET | MID-PT | ONSET | MAX | ONSET | MAX |
| P95 | **7a** | -16.1 | -12.6 | 0.9 | 4.8 | 90.0 | 98.0 |
| P96 | **12d** | -3.5 | -1.3 | - | - | - | - |
| P97 | **12a** | -14.8 | -10.6 | - | - | - | - |
| P98 | **12e** | -9.6 | - 7.5 | - | - | - | - |
| P99 | **12b** | -17.2 | -15.3 | - | - | - | - |
| P100 | **12c** | -24.9 | -24.3 | - | - | - | - |

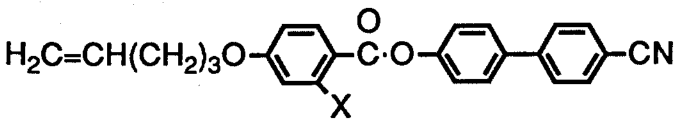
The cyanobiphenylyl ester system, however, proved to be different (Table 4.21). The parent polymer (P101), R = H, is purely smectic, but the effect of the introduction of a lateral alkyl chain (X = $OC_2H_5$, $OC_4H_9$, $OC_6H_{13}$, $OC_8H_{17}$) has transformed the system to one that is purely nematic. The effect where simple ($CH_3$, $C_2H_5$ etc.) lateral substituents have been incorporated into the mesogenic units of SCLCP in order to obtain nematogens has been previously reported [4], but these effects of long alkyl chains are new. It is hoped that this novel concept of having these long lateral alkyl chains shield the terminal polar groups from being able to form pairwise antiparallel correlations in polymeric systems may have been achieved. The first additional ethyl group in the lateral chain reduces the clearing point by 61 °C (moving from P102 to P103), but the differences then decrease. As shown in Figure 4.22, after X = $OC_4H_9$ the nematic clearing temperatures fall steadily on ascending the homologous series, each additional ethyl substituent depressing the transition temperature by *ca.* 20 °C.

It is clear therefore that phase formation is possible with a lateral alkyl chain, i.e., the lateral substituent is able to lie along the long axis of the mesogenic side chain, filling space and possibly 'lubricating' the system, and effectively suppressing smectic properties. The early members of the homologous series of lateral chains have a major effect in separating the aromatic cores. However with longer chain lengths, the lateral attachment can adopt a conformation along the molecular long axis rather than across it, and the reductions in phase transition temperatures are smaller than before.

However it should be noted that a phase was still observed when the lateral alkyl chain used was a 2-methylbutyl group (P106). This polymer had Tg = 1.1 °C and a clearing temperature at 72.6 °C. Relative to polymer P103 with X = $OC_4H_9$-n, the presence of the additional methyl branch brings about an expected decrease in temperature (28.4°C). However, the thermal stability of the phase was sufficiently high to make it strongly enantiotropic above Tg. Polymer P106 was therefore cholesteric and is novel in the sense that the chiral centre rather than being in the common location of a terminal alkyl chain is attached to the core as a lateral substituent.

## *Table 4.21*

*Phase transition temperatures and enthalpies of clearing for terminally attached SCLCP with long lateral aliphatic substituents derived from side chain precursors given in Appendix to Section 4.5*



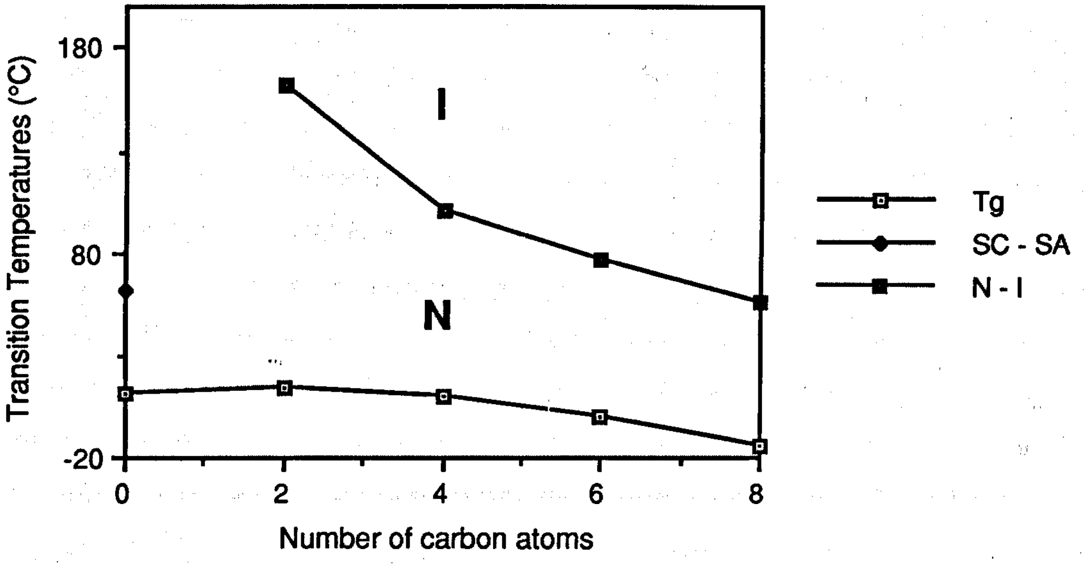
| | | Tg<br>t/°C | | $S_C$ - $S_A$<br>t/°C | | N - I<br>t/°C | |
|---|---|---|---|---|---|---|---|
| | | ONSET | MID-PT | ONSET | MAX | ONSET | MAX |
| P101 | **8** | 9.5 | 10.8 | 58.0 | 62.0 | - | > 250[A] |
| P102 | **13a** | 9.7 | 14.5 | - | - | 158.5 | 162.0 |
| P103 | **13b** | 8.6 | 9.0 | - | - | 95.4 | 101.0 |
| P104 | **13f** | -2.1 | -0.1 | - | - | 76.3 | 78.0 |
| P105 | **13c** | -18.3 | -13.7 | - | - | 54.0 | 56.0 |
| P106 | **13g** | -2.0 | 1.1 | - | - | 68.4 | 72.6 * |

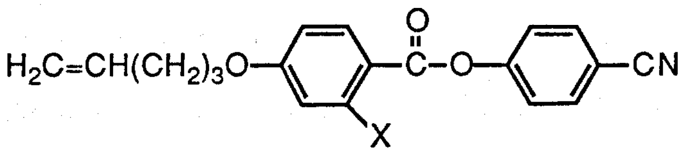
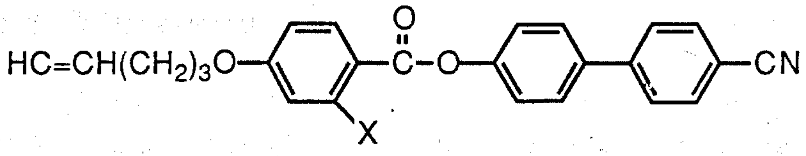
A : Smectic A-isotropic transition.

* : Chiral nematic-isotropic transition.

## *Figure 4.22*

*Effect of long lateral aliphatic substituents on terminally attached SCLCP with novel cyanobiphenylyl ester side chains*



| **Cmpd No** | **X** | **K - N, I** | **N - I** |
|---|---|---|---|
|  | | | |
| **7a** | H | 77.0 | 77.8 |
| **12d** | $OCH_3$ | 89.8 | - |
| **12a** | $OC_2H_5$ | 54.0 | - |
| **12e** | $OC_3H_7$ | 72.7 | - |
| **12b** | $OC_4H_9$ | 68.7 | - |
| **12c** | $OC_8H_{17}$ | 41.4 | - |
|  | | | |
| **8** | H | 108.0 | 264.5 |
| **13a** | $OC_2H_5$ | 100.6 | 107.6 |
| **13b** | $OC_4H_9$ | 103.7 | (65.0) |
| **13f** | $OC_6H_{13}$ | 83.4 | (43.8) |
| **13c** | $OC_8H_{17}$ | 58.5 | (38.8) |
| **13g** | $OCH_2CH(CH_3)C_2H_5$ | 81.2 | (40.5)* |

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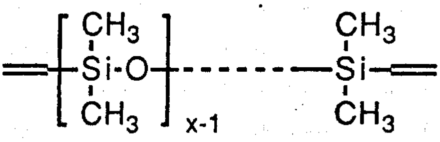
* Chiral nematic-isotropic transition.

## 4.6 ELASTOMERS

By extending the features of classical polymer chemistry to SCLCP, linear polymers may be chemically cross-linked, using a suitable agent, to give liquid crystal elastomers. Due to the network of polymer chains that is formed, the macro-Brownian motions of the backbones are restricted and this leads to a form-retaining material. However, as the micro-Brownian motions of the side chains are hardly influenced by the cross-linked polymer chains, the liquid crystalline properties are maintained. A combination of these attributes gives rise to a host of new materials, which have properties of shape and elasticity, as well as liquid crystallinity. Furthermore, macroscopic alignment may be achieved, not only by magnetic or electrical means, but also by mechanical stress. Applied deformations to the polymer network lead to the macroscopic orientation of the liquid crystalline side chains through the entire sample. This effectively curtails the unrestrained conformations of the main chain, and causes a deviation from the statistical chain conformation, in favour of an anisotropic arrangement of the polymer main chain. The director of the side chains becomes, as a result, uniformly ordered with respect to the direction of the external stress.

Following the excellent work of Finkelmann *et al.*, whose efforts have led to the possibility of commercial applications of liquid crystal elastomers in opto-electronics [56], it was considered interesting to produce a number of cross-linked laterally attached SCLCP. The objectives were to investigate both the influence of the cross-linking agent, through varying the percentage introduced to form the elastomeric network, and of change in the length of the flexible cross-linking agent used. With respect to the latter aim, two siloxane cross-linking agents, with vinylic functions at each end, were synthesised and obtained from Dr R.D.C. Richards (York Polymer Group); these had the general structure:



$$=\!\!-\left[\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{-Si-O-}\\ |\\ \mathrm{CH_3}\end{array}\right]_{x-1}\text{- - - - - - -}\begin{array}{c}\mathrm{CH_3}\\ |\\ \mathrm{-Si-}\\ |\\ \mathrm{CH_3}\end{array}\!\!-\!\!=$$

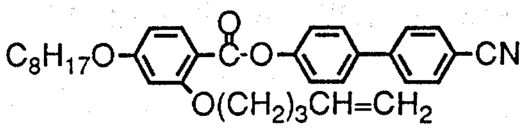
x = 16, 20

The liquid crystal elastomers were prepared through the introduction of the cross-linking agent, in the required mol-%, into the side chain precursor **5a**, and the use of this as a statistical mixture in the poly(hydrosilylation) reaction; the progress of the reaction was monitored and the product purified in the normal way. It was observed that with an increased concentration of cross-linking agent (10%), the resultant polymers were not as readily soluble in dichloromethane as their analogues prepared with a smaller concentration (5%) of cross-linker, but this did not pose a major problem. The transition temperatures and molar constituents of the polymers produced in this section are recorded in Table 4.22.

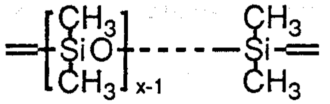
It is apparent from these results that where liquid crystallinity is observed, both glass transition and isotropisation temperatures are significantly reduced from those recorded for the linear material (W6). These suppressions in temperature are due to the softening effect of the cross-linking agent, which dilutes the mesophase. Consequently, when one compares the use of two cross-linkers of different length, **X16** and **X20**, the latter, with an additional four siloxane units, has the effect of further lowering the N - I transition temperature by 8.3 °C, i.e., by increasing the dimethylsiloxane content of the polymer network, the concentration of mesogenic units is diluted [29]. The interactions between the side chains and therefore the mesophase thermal stability are reduced, and this is reflected in the lower clearing temperature. However, it is interesting to note that the glass transition temperatures are unchanged for the two preparations W107 and W109. As the polymer chains are now held in place, due to the cross-linked nature of the network, the influence of the bulky mesogenic moieties in hindering the mobility of the main chain segments is minimised. As such, the glass transition temperatures (a polymer characteristic) of the liquid crystal elastomers are largely unaffected by the different lengths of cross-linking agent used, whereas the phase transition temperatures (a liquid crystal property) are found to be strongly dependent.

*Table 4.22*

*Phase transition temperatures and enthalpies of clearing for laterally attached side chain liquid crystalline elastomers*



**5a**



x = 16, 20

**X16, X20**

| | Alkenes mol-% | | | | Tg t/°C | | N - I t/°C | | ΔH cal/g |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | ONSET | MID-PT | ONSET | MAX | |
| W6 | 5a | 100 | **X16/20** | 0 | 28.7 | 29.4 | 84.6 | 89.8 | 0.24 |
| W107 | 5a | 95 | **X16** | 5 | 16.5 | 17.0 | 59.2 | 61.2 | 0.04 |
| W108 | 5a | 90 | **X16** | 10 | - | - | - | - | - |
| W109 | 5a | 95 | **X20** | 5 | 15.8 | 17.2 | 50.3 | 52.9 | 0.01 |
| W110 | 5a | 90 | **X20** | 10 | - | - | - | - | - |

Furthermore, it appears that larger percentages of cross-linking agent transform the polymers into rubbery materials. The elastomers are now so ordered that the side chains are not able to align anisotropically and they exhibit no mesophases. This is seen in both cases W108 and W110, where 10 mol-% of cross-linking agent has been used, regardless of its length (Table 4.22). Thermal analysis failed to show any sign of liquid crystalline properties and even the glass transition temperatures were not distinguishable within the temperature range investigated (from -50 °C up to 100 °C). When studied microscopically, the preparations were found to be distinctly elastic and rubbery, they could even be stretched, but they simply crumbled and decomposed when heated. This was in contrast to the other two samples, which exhibited the sandy birefringent nematic texture after only a few minutes of sample annealing; they then cleared at the temperatures recorded by thermal analysis (DSC). The transitions occurred over a surprisingly narrow temperature range. Despite reports of liquid crystal elastomers having been prepared with up to 20% of cross-linking chains [57], it is clear that this is not a general rule. It would seem therefore that the amount of cross-linking agent that can be used in the preparation of liquid crystal elastomers, such that both viscoelastic and liquid crystalline properties are maintained, is variable and specific to a particular system.

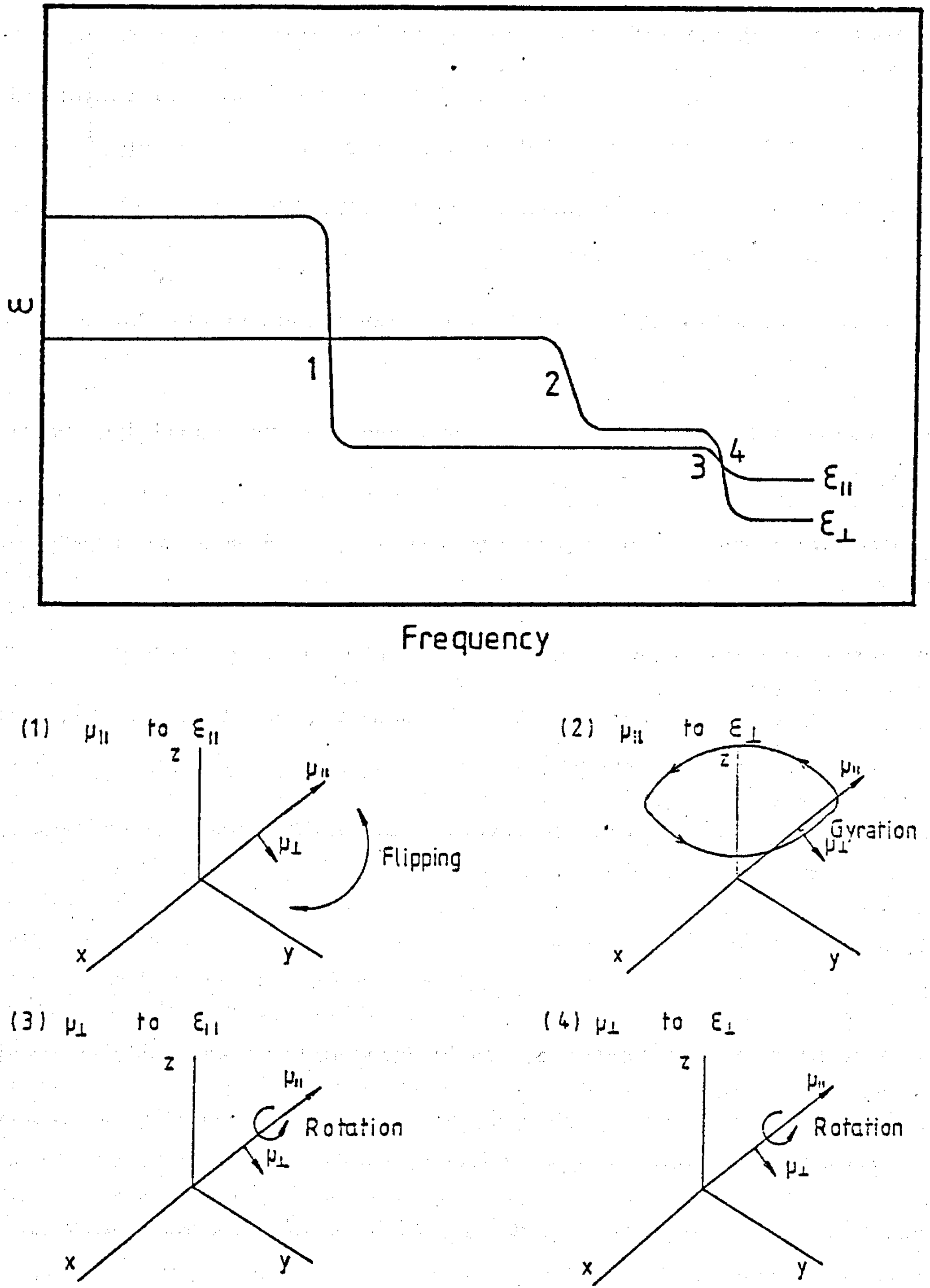
## 4.7 DIELECTRIC PERMITTIVITY STUDIES

The main aim of this project was to extend the knowledge base on side chain liquid crystal polymers by the synthesis and study of novel systems; a secondary aim was to produce polymers with high positive dielectric anisotropies as these were seen to have most potential for applications. This latter aim was approached by the use of cyano end-groups, since these would bestow a strong longitudinal dipole upon the side groups. However, short range dipole-dipole interactions have been shown to exist for such materials of LMM, resulting in antiparallel ordering of the molecular dipoles [12]. These associations significantly reduce the dipole contributions to the dielectric permittivities [13]. Both x-ray studies and permittivity measurements have indicated that this antiparallel local ordering, characteristic of terminal cyano nematics, can be suppressed by the addition of terminal non-polar nematogens [14]. This technique was applied in a similar way in these investigations on polymeric systems, through the statistical appendage of lateral side chains carrying either polar or non-polar terminal substituents to the same polymer backbone. In order to establish the effectiveness of this approach and understand the role of pairwise correlations in cyano-terminal SCLCP, measurement of the dielectric permittivities of these polymers was clearly important. This work was performed at the Royal Signals and Radar Establishment by Dr D.G. McDonnell and his colleagues, but the experiments and the interpretation of the results were made difficult by problems concerning the alignment of the polymers on substrates.

The dielectric permittivities were determined from the capacitance of a thin (25μm) parallel plate capacitor surrounded by a guard electrode and measured empty and then filled with the liquid crystal polymer. The permittivities of the polymers were then studied as a function of frequency and temperature. Nematogens (with positive dielectric anisotropy) exhibit dielectric relaxations at varying frequencies associated with the different rotational motions of the molecules (Figure 4.23). Over the frequency range studied, a single relaxation was observed in the case of each polymer and this was associated with the longitudinal dipolar contributions to either the isotropic or parallel

*Figure 4.23*

*Dielectric spectrum and relaxation modes of positive Δε nematogen*



z direction = nematic director (n)

permittivities. At frequencies below this relaxation, the isotropic permittivity values were found to be in the right order for the polar homopolymers (11 - 12), the non-polar homopolymers (4 - 4.5) and the copolymers (6.5 - 8). During this work, it was discovered that with these particular polymers, it was difficult to obtain the good, planar alignment that is essential to obtain accurate values for the magnitude of the permittivity perpendicular to the director. As a result, the dielectric anisotropy ($\Delta\varepsilon$) could not be determined practically. An alternative approach had to be found to ascertain whether antiparallel correlations had in fact been diminished by appending non-polar side chains onto the same backbone as that with terminal cyano mesogenic groups.

As antiparallel correlations exist even when a material is in the isotropic state, the isotropic permittivity values could be used to study the position. In addition, the complications brought about by the need for good sample alignment become irrelevant when the measurements conducted on the polymers involve the disordered isotropic state. However, it still had to be maintained that these values remain constant over a frequency range, i.e., before the occurrence of any dielectric relaxation. The isotropic permittivities of the side chain homopolymers and copolymers of the P(HM/DM)S backbone copolymer series were therefore obtained and these are plotted as a function of reduced temperature in Figure 4.24.

In each case, the straight line was extended backwards towards the y-axis, in order that an estimated isotropic permittivity value for a common reduced temperature, e.g., $T/T_{N\text{-}I} = 1.0$, could be obtained. These extrapolated values were re-plotted against polymer composition, expressed as an increasing percentage of non-polar side chains (Figure 4.25). The points fall along a straight line, and this linear correlation suggests the absence of antiparallel correlations for this series of polymers. This result is in agreement with that reached from Figure 4.10, i.e., based upon the effect of diluting polar groups with non-polar groups on phase transition temperatures. The conclusion arrived at was that pairwise correlations do not occur significantly in backbone copolymer systems, and the same conclusion is reached here. With the system already having been diluted by non-mesogenic methyl groups distributed along the main chain of the backbone copolymer, such that not every Si atom is carrying a mesogenic side chain, the chances of antiparallel correlations occurring between statistically distributed polar end-groups must be markedly diminished.

A similar set of measurements was conducted on similar side chain copolymers derived from the PHMS homopolymer backbone, and the findings appear in Figures 4.26 and 4.27. The results are less extensive, but, as before, a straight line is indicated, suggesting again that antiparallel correlations do not exist in these backbone homopolymer systems either. This is contrary, however, to the conclusion reached on the basis of the trends with compositional change of the phase transition temperatures; these results indicated that substantial destruction of pairwise correlations occurs upon polar group dilution with non-polar mesogenic side chains (see Figure 4.1).
This assumption was of course based on the strong negative deviation from linearity that was observed.

The overall position concerning the validity of the conclusions reached from the dielectric studies must remain open to doubt, and clearly, further work needs to be done. However, it is right to point out that the permittivity data obtained from the polymers derived from the PHMS backbone -- the data which have given the conflicting result -- are themselves possibly open to most question. The extrapolations to a constant $T/T_{N\text{-}I} = 1.0$ had to be made with lines drawn through just <u>two</u> points, and the straight line in Figure 4.27 is based on only <u>three</u> points.

*Figure 4.24*

*Isotropic permittivity versus reduced temperature for side chain polymers of the P(HM/DM)S series*

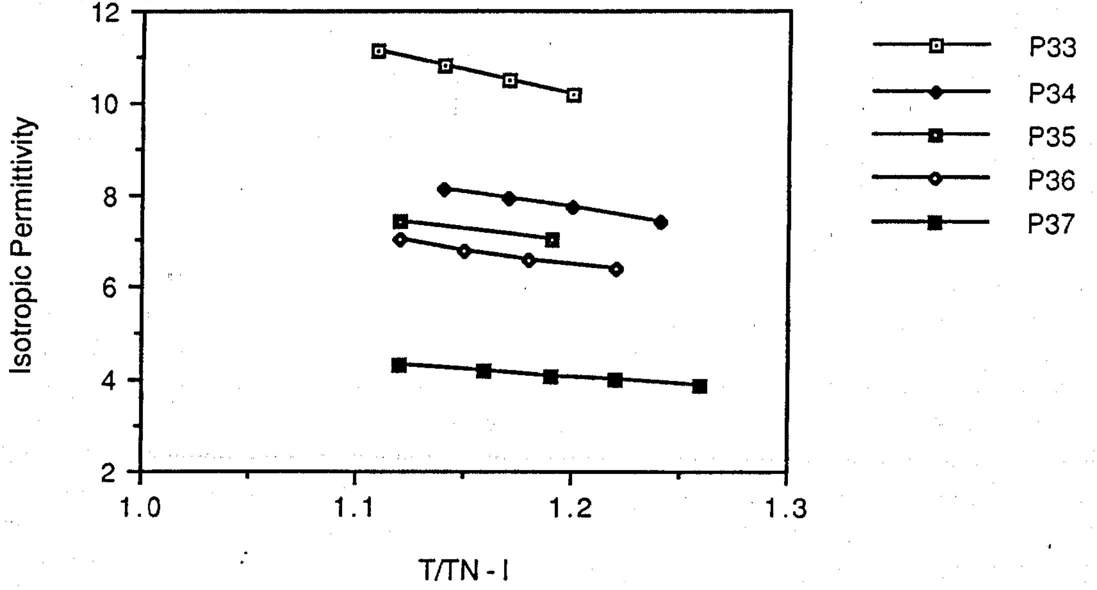


*Figure 4.25*

*Effect of polar group dilution by non-polar groups on extrapolated isotropic permittivity values for side chain polymers of the P(HM/DM)S series at $T/T_{N-I} = 1$*

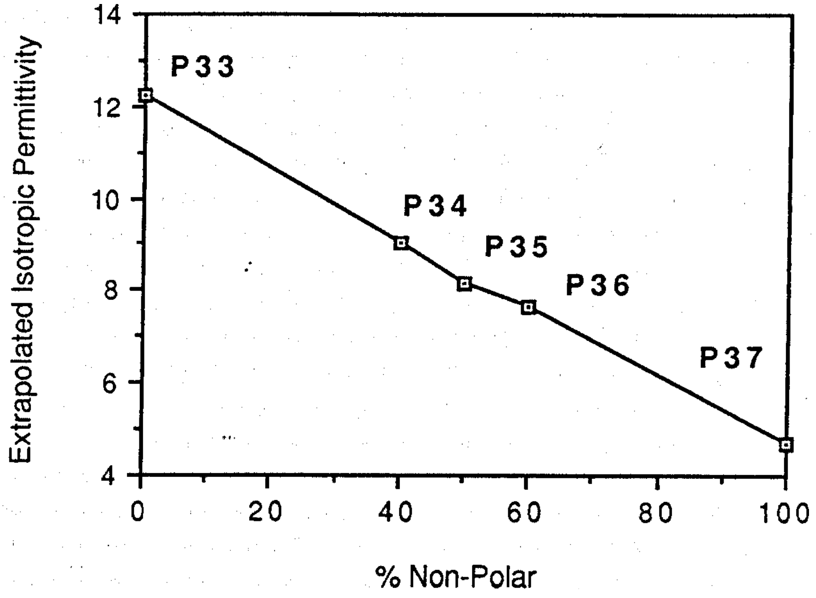


*Figure 4.26*

*Isotropic permittivity versus reduced temperature for side chain polymers of the PHMS series*

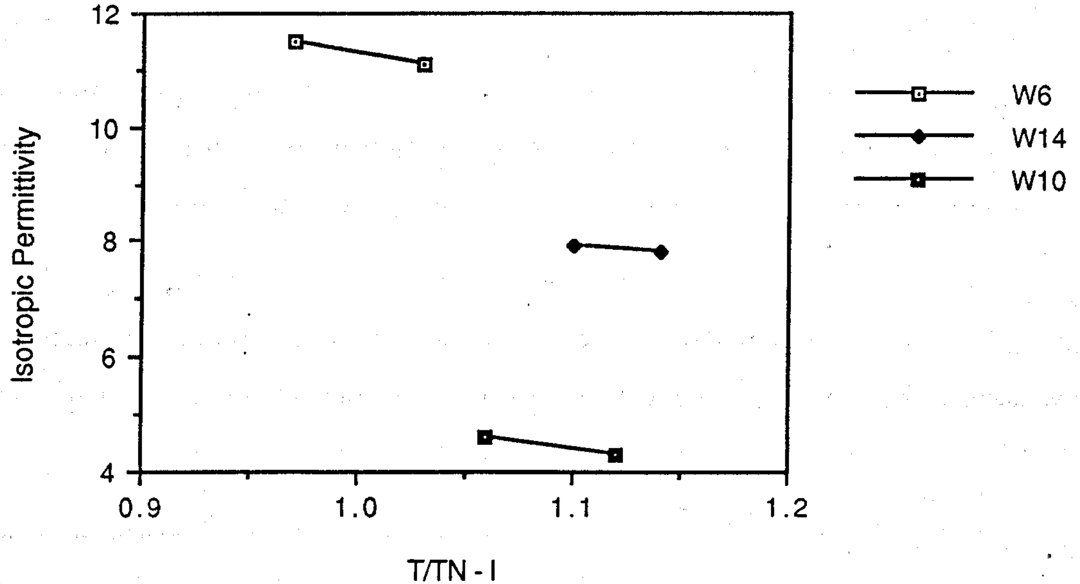
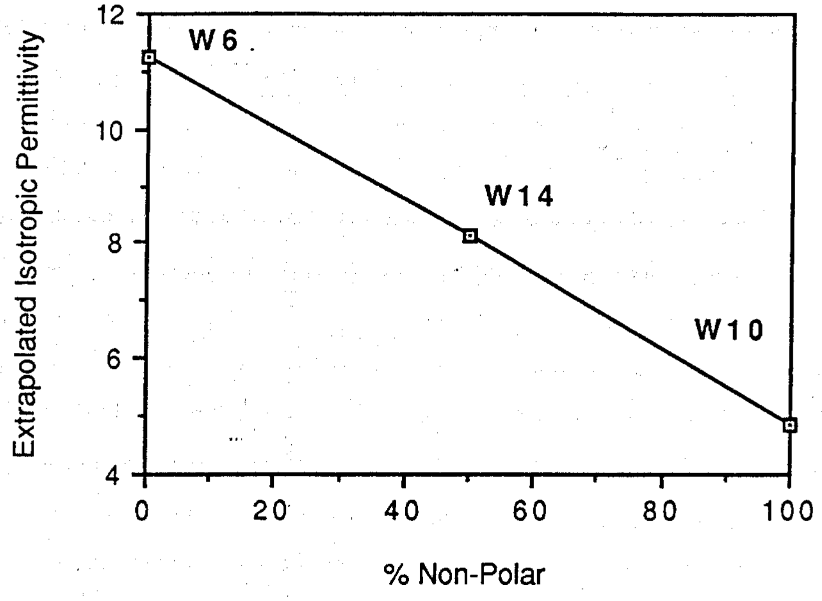


*Figure 4.27*

*Effect of polar group dilution by non-polar groups on extrapolated isotropic permittivity values for side chain polymers of the PHMS series at $T/T_{N\text{-}I} = 1$*



## 4.8 X-RAY DIFFRACTION STUDIES

The orientational order in liquid crystals can be studied using techniques such as NMR spectroscopy. However, the study of translational order, i.e., structure, requires diffraction techniques, usually involving x-rays or neutrons. Diffraction occurs when radiation is scattered from the atoms in a sample. The various scattered waves from the different atomic sites combine and, depending on the relative phases of these waves, lead to constructive or destructive interferences. As the phases of the waves depend upon the relative positions of all of the atomic sites, the diffraction in a given direction relies on the spatial distribution of the atoms in the sample. A diffraction experiment is thus able to probe the translational order within the sample, which allows for the elucidation of the sample structure [58]. In order that structural correlations between the mesogenic side chains and the polymer backbone may be understood, it was desirable that x-ray diffraction studies were performed on the laterally attached SCLCP synthesised. This work was conducted by Dr R.M. Richardson and Mr A.S. Cherodian, at the University of Bristol, on the side chain homopolymers and copolymers and their backbone copolymeric analogues whose physical properties have already been discussed in Sections 4.2.1, 4.2.2 and 4.2.4.

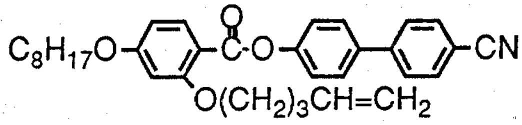
As with the investigations on dielectric properties, it was imperative that well aligned samples were obtained, in order that representative and distinguishable diffraction patterns were produced, to enable proper characterisation of the LCP structure. These orientations were achieved either by drawing fibres of the LCP from the semi-molten state, and/or by cooling a sample in a Lindemann tube from the isotropic state in a 11.5 tesla magnetic field. From the diffraction patterns, the positions of the 'OOl' meridional reflection peaks and the outer diffuse peaks (Do) suggest that the side chains in the nematic phase are orientated along the direction of the fibre axis, for the drawn fibre samples. In the case of samples aligned by magnetic field, the director orientation is along the direction of the field.

The d-spacings of the 'OOl' peak, corresponding to the longitude of the mesogenic side chain, were measured for each sample at different temperatures. The ranges of variation in the d-spacing as a function of temperature are listed in Table 4.23 for polymers of the backbone homopolymer and copolymer series. It is first noted that the magnitude of the d-spacing decreases with falling temperature for the PHMS homopolymer backbone samples, but the opposite trend or no trend is observed for polymers synthesised from the P(HM/DM)S copolymer backbone. Furthermore, the d-spacings indicate that some degree of mesogenic core overlap occurs, since the spacings recorded for the side chain homopolymers (W6, W10, W11, P33 and P37) are noticeably shorter than the lengths of 33.0 Å and 29.5 Å for the pentyl and cyano mesogenic units respectively, based upon CPK molecular models. The overlap appears to be greater for the polymers with side chains bearing pentyl end-groups. Mesogenic units rarely exist singularly, and a certain degree of overlap can usually be expected. As such, the occurrence of slight overlapping side chains at their termini is quite normal.

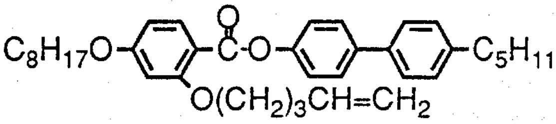
The experimental patterns are represented by the profiles of the radial scans of the 'OOl' peaks (Figure 4.28), as well as by the colour plates of the diffraction patterns (Plate 7). In both cases, four characteristic spots of the 'OOl' peak can be distinguished. This pattern is typical of those obtained from SCLCP of the backbone homopolymer type and suggests that the side chain mesogenic units adopt a quasi-layer structure, with short range correlation and a smectic C-like packing. The laterally attached side chains are envisaged as orientated parallel to the polymer backbone [52]. The bulky side chains may then exercise a steric effect on neighbouring mesogenic units and consequently force them to splay slightly away. This could explain the smectic C-like short range order indicated by the diffraction pattern. The $S_C$-like tilt may also contribute to the fact that the observed d-spacings are less than the values calculated from molecular models.
This assumption is supported to a certain extent by the observed increases in d-spacing with increasing temperature for the backbone homopolymer series. If the mesogenic units are in fact tilted with respect to one another, the tilt angle would probably be reduced on heating, since the side chains would then be energetically able to oscillate

*Table 4.23*

*The ranges of variation in the d-spacing of the 'OOl' peaks as a function of decreasing temperature for the nematic phases of some laterally attached side chain homopolymers and copolymers and their backbone copolymeric analogues*



**5a**



**5c**

| | Alkenes mol-% | | | | D-spacing/Å |
|---|---|---|---|---|---|
| *PHMS homopolymer backbone* | | | | | |
| W6 | **5a** | 100 | **5c** | 0 | 28.4 - 26.8 |
| W14 | **5a** | 50 | **5c** | 50 | 30.2 - 28.7 |
| W10 | **5a** | 0 | **5c** | 100 | 27.0 - 24.1 |
| W11 | **5d** | 100 | - | - | 26.9 - 24.5 |
| *P(HM/DM)S copolymer backbone* | | | | | |
| P33 | **5a** | 100 | **5c** | 0 | 26.2 - 27.4 |
| P34 | **5a** | 60 | **5c** | 40 | 26.5 - 28.0 |
| P36 | **5a** | 40 | **5c** | 60 | 27.4 (no visible change) |
| P37 | **5a** | 0 | **5c** | 100 | 25.1 - 25.9 |

more freely and thereby adopt a more orthogonal orientation. This subsequently enlarges the d-spacing.

For the copolymeric backbone, the mesogenic moieties are interspersed by non-mesogenic methyl groups along the polymer main chain. As the side chains are now further apart, steric interactions should be less significant. The smectic C-like short range order effect is now considerably smaller. This is seen in the radial scan profiles as the 'filling-up' of the troughs between the two pairs of twin peaks (Figure 4.29), to give just two broad peaks. The diffraction patterns for these polymers also reveal peaks that are more diffuse (Plate 8). With this expected reduction in short range ordering, the fluctuations of the mesogenic units about the axis should be smaller at higher temperatures, and smaller increases in d-spacing would have been anticipated. In fact, small decreases are found in three of four cases (Table 4.23). It is possible that this arises from greater side chain overlap as molecular movement increases with temperature.

The tilt-angles for the polymers bearing either terminal polar or non-polar groups are very similar, 17° ± 2° for the cyano end-group and 19° ± 2° for the pentyl. Furthermore, an increase in the length of the flexible spacer by one $CH_2$ unit is accompanied by an increase in the observed tilt angle to 22° ± 2°, with an associated decrease in 'OOl' d-spacing; the values quoted in Table 4.23 are for the terminal pentyl side chain LCP. Both the diffraction patterns and the radial scans for the longer spacer LCP W11, derived from the PHMS homopolymer backbone, exhibit properties that are even more typical of smectic C-like structure (Figure 4.30 and Plate 9), with the spots and peaks apparently further apart.

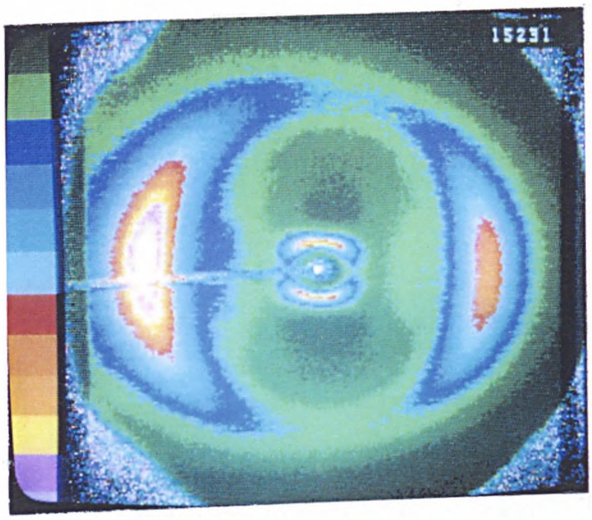


**Plate 7**

*Typical diffraction pattern for laterally attached SCLCP of the PHMS series*

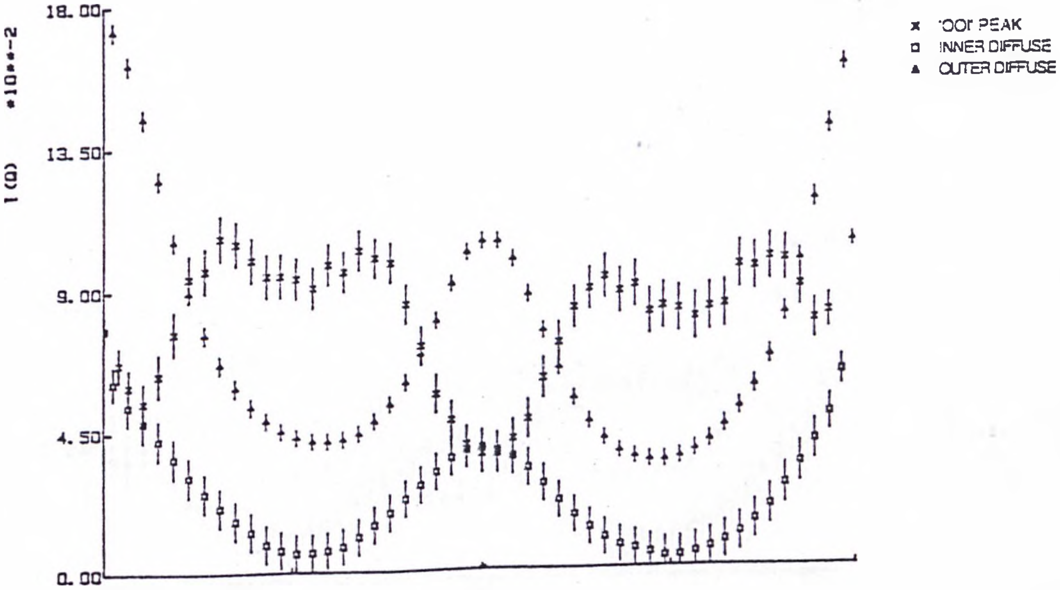


**Figure 4.28**

*Typical radial scan of the 'OOl' peaks for laterally attached SCLCP of the PHMS series*

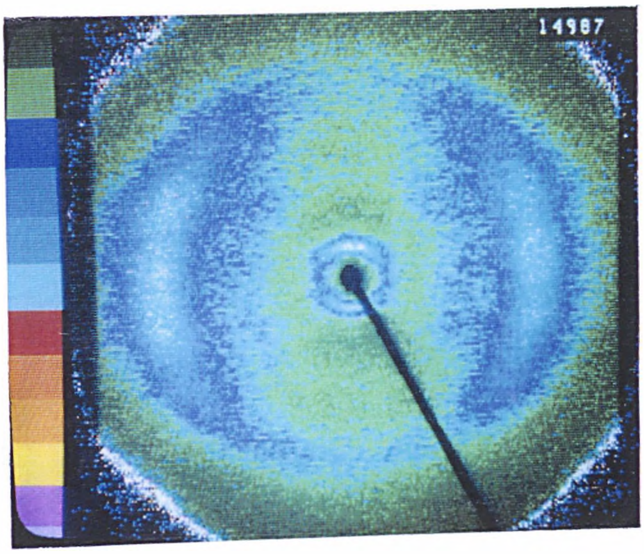


**Plate 8**

*Typical diffraction pattern for laterally attached SCLCP of the P(HM/DM)S series*

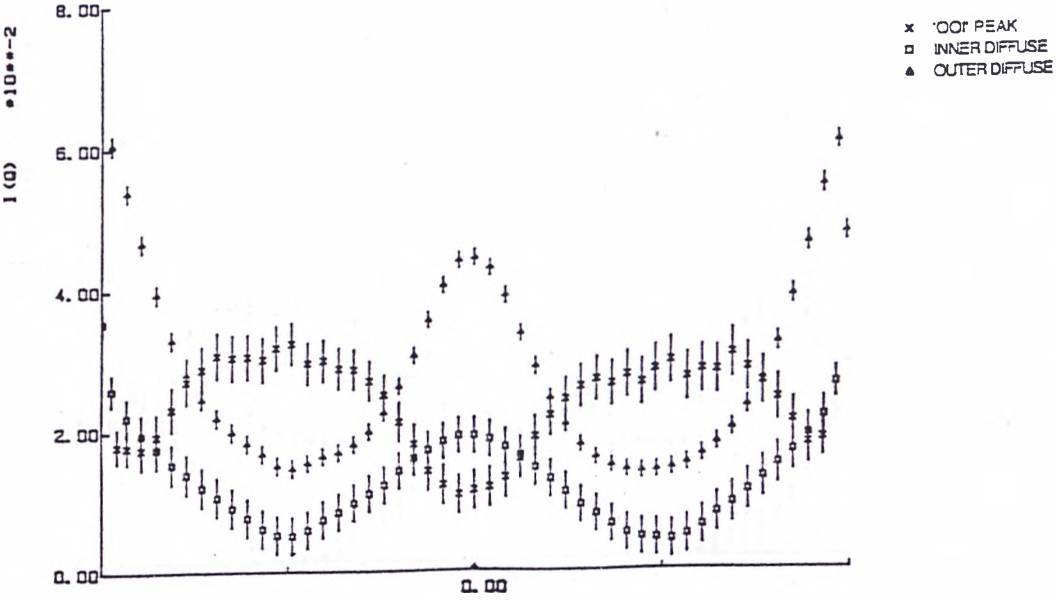


**Figure 4.29**

*Typical radial scan of the 'OOl' peaks for laterally attached SCLCP of the P(HM/DM)S series*

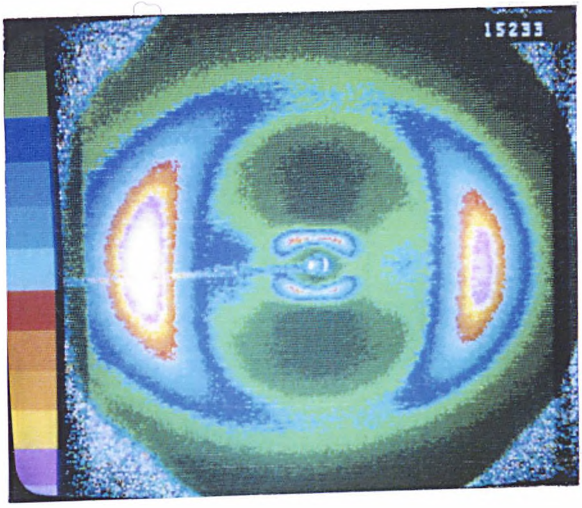


***Plate 9***

*Diffraction pattern for the laterally attached SCLCP of the PHMS series with the longer spacer (W11)*

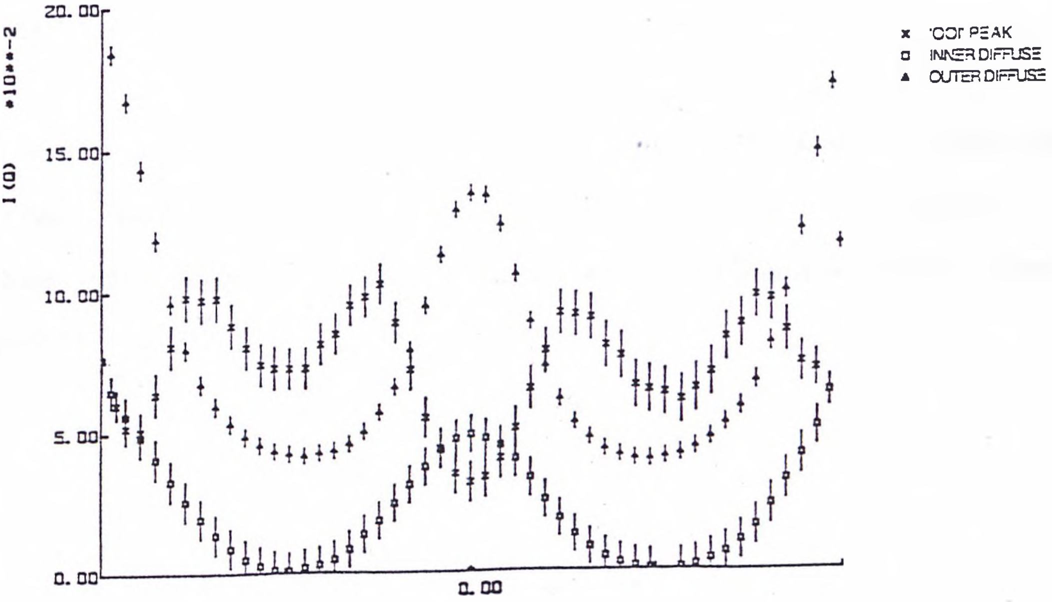


***Figure 4.30***

*Effect of changing spacer length on the radial scan of the 'OOl' peaks for the laterally attached SCLCP of the PHMS series*

The diffraction patterns show a further two types of peak, an outer diffuse peak and an inner diffuse peak. The outer diffuse peak (4 - 4.5 Å) corresponds to the soft side-to-side packing of the mesogenic groups, i.e., the breadth of the molecule. These values are all virtually identical, as would be expected from side chains which only differ in the nature of the terminal group.

The identification of the inner diffuse peak, however, is less clear. It is thought that this distance, which ranges from 8 - 9 Å, may be associated with the flexible spacer. This distance is found to increase when results for samples with the five spacer and the homologue with the six spacer are compared. The lengths of the flexible spacers calculated from CPK models are 7.6 Å and 8.8 Å for five and six methylene units respectively. However, observed irregularities in the repeat distance obtained from the diffraction patterns make this assignment tentative, and experiments are continuing in this area with infra-red dichroism and neutron scattering studies using partly deuteriated versions of these samples, in order to test this proposal. There is, however, no observed diffraction peak that can be associated with the polymer backbone.

Incomplete as these x-ray diffraction studies may be, it is hoped that the information that has been obtained will encourage others in the field to study their LCP in a similar manner and extend the fundamental knowledge base on structural aspects of side chain polymers in general.

## 4.9 REFERENCES

1. H.J. Coles, *Faraday Discuss. Chem. Soc.*, **79**, 201 (1985).
2. C.B. McArdle, M.G. Clark, C.M. Haws, M.C.K. Wiltshire, A. Parker, G. Nestor, G.W. Gray, D. Lacey and K.J. Toyne, *Liq. Cryst.*, **2**, 573 (1987).
3. H. Finkelmann, U. Kiechle and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **94**, 343 (1983).
4. P.A. Gemmell, G.W. Gray and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **122**, 205 (1985).
5. H. Finkelmann, in *"Polymer Liquid Crystals"* (eds. A. Ciferri, W.R. Krigbaum and R.B. Meyer), Academic Press, New York (1982).
6. F. Hessel and H. Finkelmann, *Polym. Bull. (Berlin)*, **14**, 375 (1985).
7. Q.F. Zhou, H.M. Li and X.D. Feng, *Mol. Cryst. Liq. Cryst.*, **155**, 73 (1988).
8. H. Finkelmann and G. Rehage, *Makromol. Chem., Rapid Commun.*, **1**, 31 (1980).
9. G. de Marignan, D. Teyssie, S. Boileau, J. Malthète and C. Noel, *Polymer*, **29**, 1318 (1988).
10. G. Nestor, Ph.D. Thesis, University of Hull (1988).
11. H. Finkelmann, H.J. Kock and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **89**, 23 (1982).
12. A.J. Leadbetter, R.M. Richardson and C.N. Colling, *J. Phys. (Paris)*, **36**, 37 (1975).
13. D.A. Dunmur, M.R. Manterfield, W.H. Miller and J.K. Dunleavy, *Mol. Cryst. Liq. Cryst.*, **45**, 127 (1978).
14. M.J. Bradshaw and E.P. Raynes, *Mol. Cryst. Liq. Cryst.*, **91**, 145 (1983).
15. G.W. Gray, *"Molecular Structure and the Properties of Liquid Crystals"*, Academic Press, London and New York (1962).
16. Hp. Schad and M.A. Osman, *J. Chem. Phys.*, **79**, 5710 (1983).
17. L.K.M. Chan, G.W. Gray, D. Lacey, T. Srithanratana and K.J. Toyne, *Mol. Cryst. Liq. Cryst.*, **150**, 335 (1987).
18. F. Hardouin, G. Sigaud, P. Keller, H. Richard, H.T. Nguyen, M. Mauzac and M.F. Achard, *Liq. Cryst.*, **5**, 463 (1989).
19. X.J. Wang and M. Warner, *J. Phys. A, Math. Gen.*, **20**, 713 (1987).
20. H. Stevens, G. Rehage and H. Finkelmann, *Macromolecules*, **17**, 851 (1984).
21. W.D. Hawthorne, Ph.D. Thesis, University of York (1986).
22. R.D.C. Richards, J. Hollingshurst, M.S.K. Lee, J.A. Semlyen and G.W. Gray, in preparation.

23. F. Hardouin, S. Mery, M.F. Achard, M. Mauzac, P. Davidson and P. Keller, *Liq. Cryst.*, **8**, 565 (1990).

24. S.J. Clarson, K. Dodgson and J.A. Semlyen, *Polymer*, **26**, 930 (1985).

25. T. Sagane and R.W. Lenz, *Polymer*, **30**, 2269 (1989).

26. T.G. Fox and P.J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

27. K. Ueberreiter and G. Kannig, *J. Colloid Sci.*, **7**, 569 (1952).

28. J. Frenzel and G. Rehage, *Makromol. Chem.*, **184**, 1685 (1983).

29. H. Ringsdorf and A. Schneller, *Makromol. Chem., Rapid Commun.*, **3**, 557 (1982).

30. G. Nestor, G.W. Gray, D. Lacey and K.J. Toyne, *Liq. Cryst.*, **6**, 137 (1989).

31. G.W. Gray, J.S. Hill, D. Lacey and M.S.K. Lee, *Proc. 13th Int. Liq. Cryst. Conf., Vancouver*, Abstract POL-53 (1990).

32. G. Nestor, unpublished results.

33. H. Ringsdorf, H.W. Schmidt and A. Schneller, *Makromol. Chem., Rapid Commun.*, **3**, 745 (1982).

34. P.J. Flory, *"Principles of Polymer Chemistry"*, Cornell Univ. Press, New York (1953).

35. O. Olabisi, L.M. Robeson and M.T. Shaw, *"Polymer-Polymer Miscibility"*, Academic Press, London and New York (1979).

36. S. Ambrosino and P. Sixou, in *"Microemulsions and Liquid Crystals"* (ed. M.A. El-Nokaly), ACS Symposium Series, No. 384, Washington DC (1989).

37. H. Benthack-Thoms and H. Finkelmann, *Makromol. Chem.*, **186**, 1895 (1985).

38. C. Casagrande, M. Veyssie and H. Finkelmann, *J. Phys. (Paris)*, **43**, L671 (1982).

39. G.W. Gray and A. Mosley, *J. Chem. Soc., Perkin Trans. II*, 97 (1976).

40. W.H. de Jeu, J. Van der Veen and W.J.A. Goossens, *Solid State Commun.*, **12**, 405 (1973).

41. D. Demus and H. Zaschke, *"Flüssige Kristalle in Tabellen"*, Vol. II, VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig, German Democratic Republic (1984).

42. G.W Gray, J.S. Hill and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **197**, 43 (1991).

43. G.W. Gray and D.G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **34**, 211 (1977).

44. G.W. Gray and P.A. Windsor, *"Liquid Crystals and Plastic Crystals"*, Vol. 1, Ellis Horwood, Chichester (1974).

45. L.K.M. Chan, Ph.D. Thesis, University of Hull (1987).

46. D. Coates and G.W. Gray, *Mol. Cryst. Liq. Cryst.*, **37**, 249 (1976).

47. Hp. Schad and S.M. Kelly, *J. Chem. Phys.*, **81**, 1514 (1984).

48. G.W. Gray, M. Hird, D. Lacey and K.J. Toyne, *Mol. Cryst. Liq. Cryst.*, **172**, 165 (1989).

49. G.W. Gray, J.S. Hill, D. Lacey, M.S.K. Lee, G. Nestor, K.J. Toyne and M.S. White, *Proc. 12th Int. Liq. Cryst. Conf., Freiburg*, Abstract P003 (1988).

50. G.W Gray, J.S. Hill and D. Lacey, *Angew. Chem. Adv. Mater.*, **101**, 1146 (1989).

51. A. Nazemi, E.J.C. Kellar, G. Williams, F.E. Karasz, J.S. Hill, D. Lacey and G.W. Gray, *Liq. Cryst.*, **9**, 307 (1991).

52. F.J. Bormuth and W. Haase, *Liq. Cryst.*, **3**, 881 (1988).

53. P. Keller, F. Hardouin, M. Mauzac and M.F. Achard, *Mol. Cryst. Liq. Cryst.*, **155**, 171 (1988).

54. W. Weissflog and D. Demus, *Crystal Res. Technol.*, **19**, 55 (1984).

55. S. Takenaka, H. Morita, S. Kusabayashi, Y. Masuda, M. Iwano and T. Ikemoto, *Chem. Lett.*, 1559 (1988).

56. H. Finkelmann, *Angew. Chem. Int. Ed. Engl.*, **27**, 987 (1988).

57. R. Zentel, G. Reckert and B. Reck, *Liq. Cryst.*, **2**, 83 (1987).

58. A.J. Leadbetter, in *"The Molecular Physics of Liquid Crystals"* (eds. G.R. Luckhurst and G.W. Gray), Academic Press, London (1979).

# five

# *conclusions*

# 5. CONCLUSIONS

An early objective of this work was to develop a reliable and reproducible method for the preparation of laterally attached side chain liquid crystal polysiloxanes (SCLCP). This has been well investigated and Sections 2.2.3 to 2.2.5 cover the techniques involved in the polymer modification reaction -- from the monitoring of reaction progress, through to the purification of the final polymer. Other factors which have been examined include the effect of using different reaction solvents in the hydrosilylation process and the use of column chromatography for purification of the final products.

Most significantly, these findings have thrown some light on the relative efficiencies of different platinum catalysts. Earlier workers at Hull had successfully prepared LCP with terminally linked side chains by using hexachloroplatinic acid as the catalyst. In this work, the hydrosilylation process involved mesogenic groups designed for lateral appendage, and it was found that anomalous α-addition of hydrogen at the double bond was occurring with this catalyst. The anomalous α-addition had not been observed in the previous studies on terminally attached SCLCP, a fact confirmed in these investigations (Section 4.2.4). The change in catalyst to platinum divinyltetramethyldisiloxane complex (PVMS) had many advantages. Anomalous α-addition was no longer a problem, and consequential upon this prevention of anomalous addition product formation, there was an observed significant increase in the phase transition temperatures of the polymers prepared with PVMS compared to their equivalents synthesised using hexachloroplatinic acid (Section 4.2.1).

The dependence of phase transition temperatures on molecular weight and on polydispersity is shown in Section 4.2.4 to be an extremely important consideration in the synthesis of both terminally and laterally attached SCLCP. From the studies of three systems, including work of this nature on laterally attached SCLCP for the very first time, the trend of rising phase transition temperatures with increasing molar mass has been consistently observed. These transition temperatures become approximately constant only at about $\overline{DP}$ 100. For a polymer of finite molar mass, one may relate to the glass temperature at the limiting value for infinite molar mass by mathematical expressions. From the present study for the laterally attached SCLCP, such calculated values agree very well with the experimental data for $\overline{DP} > 100$, thus supporting the literature claims of limiting transition temperature values. Collectively, these findings stress the importance of having well characterised samples, and emphasize that important parameters ($\overline{DP}$, $\overline{Mw}$, $\overline{Mn}$, $\gamma$) must be quoted together with thermal data to enable meaningful comparisons to be made between different SCLCP.

An important aim of this project was to obtain laterally attached SCLCP which exhibit room temperature nematic phases with high positive dielectric anisotropies. In order to maximise the dielectric properties of the polymers, side chain copolymers were derived where non-cyano-substituted and cyano-substituted mesogenic groups were appended as a statistical distribution of side chains along a preformed backbone. It was envisaged that the non-polar groups would prevent both intra- and inter- molecular associations of the polar end-groups and therefore reduce the antiferroelectric short range ordering.

This is believed to have been achieved (Section 4.2.2), as progressive terminal polar group dilution by non-polar groups has been observed to give a strong negative deviation from a linear dependence of $T_{N-I}$ on increasing non-polar content, suggesting extensive break up of pairwise antiparallel correlations. When the same study was repeated with the P(HM/DM)S copolymer backbone (Section 4.2.5), no real minimum could be distinguished from the plot of the results. In this case, there is statistically a smaller chance of pairwise correlations occurring in a system that has already been diluted by the non-polar methyl groups on the backbone. As not every Si is carrying a mesogenic group, regardless of whether this is a terminal polar or non-polar group, it is hardly surprising that the effect is not as dramatic as before.

The aim of reducing pairwise correlations was then extended by the synthesis of terminally attached SCLCP, with long aliphatic chains laterally substituted on the mesogenic group (Section 4.5). The lateral substituent is able to distort itself to lie along the molecular long axis, producing a molecule of elongated shape compatible with the side chains being able to pack and exhibit the nematic phase. Although the observed reductions in thermal properties suggest that advantageous increases in the dielectric anisotropy may have been achieved, this has not yet been confirmed experimentally by dielectric permittivity measurements. It is hoped, however, that the long lateral substituent chains can shield the terminal polar groups from forming pairwise antiparallel correlations, thereby introducing a new and novel approach towards enhancing the dielectric properties of cyano-containing mesogenic systems.

The effect of changing backbone flexibility on phase transition temperatures was examined for laterally appended SCLCP derived from the P(HM/DM)S backbone through comparisons with their backbone homopolymer analogues (Section 4.2.5). The difference in backbones was found not to affect the phase type, but significant reductions in transition temperatures were observed, a consequence of 'diluting' the mesogenic groups along the backbone with non-mesogenic segments. Furthermore, it is noted that the increased backbone flexibility has acted against the molecular ordering in the nematic phase, as inferred from the reduced enthalpy values for the N - I transitions for the backbone copolymer systems.

The work pioneered within this Group on mixed copolysiloxane systems which contain both terminally and laterally appended side chains on the same backbone has been much further explored (Section 4.4). The use of a variety of interesting end-groups, sited on either the terminal or lateral component, has enabled a broader understanding of this effective means of obtaining liquid crystalline polymers with required properties.

From these results, it has also been possible to formulate a hypothesis as to the possible configurations adopted by these lateral/terminal systems, and by other laterally attached SCLCP prepared in this work. In the mixed copolysiloxanes, the introduction of large amounts (up to 70%) of terminally attached mesogenic groups can be used without significantly affecting the thermal properties and nematic ordering of the laterally attached homopolymer. Conversely, the smectic phase normally exhibited by the terminally attached homopolymer is noticeably absent from the copolymers which have above a 30% composition of lateral side chain. The change in phase type from smectic to nematic may be associated with a gradual alteration in backbone orientation from the oblate form to a prolate form; the preferred conformation is possibly controlled by the entropy of the system. This theory is to some extent substantiated by the dielectric studies conducted on these copolymer systems, when a change in sign of the dielectric anisotropy from negative to positive was observed as the temperature was increased.

The model postulated for the laterally attached SCLCP on the basis of the off-centre point of spacer attachment may explain the reduced N - I transition temperatures observed exclusively for these systems on passing from monomer to polymer, an effect which is not consistent with the small increases reported for nearly all of the small number of other known laterally attached SCLCP. Furthermore, the suggested configuration of the laterally attached side chains along the backbone, supported to a certain extent by the x-ray diffraction studies conducted on these polymers, may also explain the lack of smectic properties observed in the systems reported in this work.

By altering the nature of the end-group on the side chain, or by the modification of the mesogenic core, it had been hoped that data would be obtained allowing for the development of more secure structure-property correlations for laterally attached SCLCP (Section 4.3). However the low mesophase thermal stabilities of the novel side chain precursors, a consequence of the long lateral ω-alkenyl chains which disrupt nematic packing, coupled with the unique effect of reduced transition temperatures on moving from side chain precursor to polymer, have meant that many of the SCLCP prepared were non-mesomorphic. The isotropisation temperatures of the side chain precursors have, however, allowed for the construction of a nematic terminal group efficiency order, which is in accord with several other simpler series of low molar mass mesogens. It is possible therefore that the order derived for the side chain precursors may be applicable to the polymers.

A homologous series of laterally attached SCLCP with terminal alkoxy groups was found to exhibit 'odd-even' $T_{N-I}$ alternation effects such as those observed for many other series of low molar mass mesogens (Section 4.3.1). However, it is noted that the effect is far from perfect, as a number of points appear to deviate from the idealised plot of $T_{N-I}$ against chain length. These findings exemplify the unpredictability of polymeric systems, and show the need to control parameters such as $\overline{Mw}$, $\overline{Mn}$, $\overline{DP}$ and $\gamma$ if proper comparisons are to be drawn between different polymers.

It was considered interesting to prepare a number of cross-linked laterally attached SCLCP, in order to investigate both the influence of the cross-linking agent, through varying the percentage introduced to form the elastomeric network, and the change in the length of the flexible cross-linking agent used (Section 4.6). The cross-linking agent, which dilutes the mesophase, has the effect of lowering N - I transition temperatures, with this effect being greater when a longer cross-linker is used. However, it is interesting to note that whereas this affected the N - I transition temperatures, the glass transition temperatures of the liquid crystal elastomers remained largely unchanged. Furthermore with larger percentages of cross-linking agent (> 10%), the polymers were transformed into rubbery materials, and no mesophases were detected.

The problem of obtaining good, planar sample alignment severely hindered the study of the dielectric properties of the polymers prepared. The magnitude of the permittivity perpendicular to the director could not be determined experimentally, and the isotropic permittivity results had to be used instead to study the position (Section 4.7).

The conclusions reached from these measurements agree with those from the studies of diluting polar side groups with non-polar side groups on phase transition temperatures for the P(HM/DM)S series of backbone copolymers. However, a conflicting result may be indicated for the PHMS backbone homopolymer system. These dielectric results are therefore not conclusive and further work will have to be done, with particular regard to obtaining parallel alignment of the polymers to the supporting surfaces. The area of dielectric permittivity measurements must be rigorously pursued, for the results from such studies are crucial in order to establish the effects of diminishing antiparallel correlations in the side chain copolymers.

From the x-ray diffraction studies, it has been possible to obtain preliminary evidence of structural correlations between the mesogenic side groups and the polymer backbone in the laterally attached SCLCP (Section 4.8). The diffraction patterns and d-spacing values suggest that the side chains adopt a quasi-layer structure, with short range correlation and a smectic C-like packing, in the backbone homopolymer systems. This short range order effect is, however, smaller in the backbone copolymer series, due to reduced steric interactions between the mesogenic moieties that are interspersed with non-mesogenic methyl groups distributed along the backbone. However, these studies are again incomplete, and further experiments with infra-red dichroism and also neutron scattering studies using partly deuteriated analogues should prove effective tools in testing the proposals put forward.

In conclusion, many observations over the course of this work have highlighted the difficulties in achieving consistency and reproducibilty of thermal data for polymer preparations. This is especially evident in the case of side chain copolymers, where local variations in side chain population on individual backbones within the bulk sample and fluctuations in side chain composition make reproducibility of transitions from batch to batch a near impossibility. This difficulty cannot be circumvented by the use of mixtures which would guarantee consistency of side chain composition in the systems (Section 4.2.6). It has also been shown that it is unwise to make sweeping generalisations about the effects upon mesophase thermal stability on passing from side chain precursor to SCLCP. These points collectively illustrate that the transition temperatures for SCLCP are affected by many more factors than those for low molar mass analogues; some of the factors are still to be understood, and many are unique to the macromolecular system and often difficult to control. However, it is felt that the results from this work have contributed to a better understanding of these systems and have broadened the knowledge base relating to laterally attached side chain liquid crystal polymers.