Synthesis of Side-Chain Liquid Crystal Polymers

by Cyclopolymerisation

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This project has involved the introduction of a new series of polymer backbones in the synthesis of side-chain liquid crystal (SCLC) polymers. This novel method involves the cyclopolymerisation of suitably substituted non-conjugated dienes to produce polymers incorporating allicyclic rings within the polymer backbone. The main advantage of this new methodology is that it has seldom been used to synthesise SCLC polymers in the past, so there is great scope for the production of new polymer systems.

The first main aim of this project was to optimise the polymerisation procedure, so as to maximise yields and optimise the molecular weight distribution. Once this had been done a programme of synthesis was undertaken to produce SCLC polymers which exhibited the SmC* phase, for use in display devices and for optical storage.

It was found with these new polydiene systems that some of the SCLC polymers produced wide SmC* phases, in the range ≈ 20 to 170 °C. Unfortunately, most of the SCLC polymers produced were of low DP.

It was found that the low molecular weight was due to degradative chain transfer to monomer by abstraction of an allylic hydrogen by the growing polymer chain. As it was thought that the low DP was affecting the alignment properties of the SCLC polymers, a variety of alternative synthetic strategies were attempted to overcome this problem. The synthesis of monomers without any allylic hydrogens, in an attempt to obtain polymers of a higher molecular weight, proved to be unsuccessful. However, a polymer system was synthesised which added evidence to support the proposed structures of the polymers and the mechanism of cyclopolymerisation.

The glass transitions of the polymers occurred near to room temperature, making them potentially useful in display devices, if they exhibit the correct phases and alignment difficulties could be overcome.

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Contents

1.1 Introduction to liquid crystals

The topic of liquid crystals is a vast subject, so only a brief introduction will be given here. Thermotropic liquid crystals produce phase changes which are dependent upon changes in temperature and this is the nature of the materials discussed in this thesis.

Thermotropic liquid crystals can be subdivided into two groups, calamitic and discotic. Discotic phases are formed by disc shaped mesogens either forming columns of molecules (columnar phases) or an arrangement not dissimilar to a pile of coins (nematic phases). For a further account of discotic liquid crystals the reader is referred to the following articles [1,2].

The remainder of this introduction will be dedicated to thermotropic calamitic liquid crystals with special mention being made to phases which are exhibited by the compounds described in this work and to devices which are both presently commercially important and to those which may become so, for which the materials prepared in this project may be used. Calamitic liquid crystals consist of long rod shaped molecules and can exhibit smectic and nematic or chiral nematic phases.

1.1.1 Basic Concepts

Under normal conditions matter can exist in one of three different states; as a solid, a liquid or a gas. In the solid state molecules have three-dimensional order and are in a fixed position as described by a crystal lattice, which only allows for small molecular vibrations. However, the molecules can rotate. In the liquid state the molecules possess unhindered rotation and translation, moving freely through the bulk, resulting in a loss of long range order. In the gaseous state the molecules move freely, in a random manner, without constraint and only occasional contact with their neighbours.

Let us consider a sample of an organic compound in the solid crystal state. If the temperature is increased, then the thermal motion of the molecules within the sample also increases and at a certain temperature, i.e., the melting point, the molecules vibrate to such an extent that the three dimensional order is lost and the sample becomes an isotropic liquid. However, this process is a very disruptive one and is not obeyed by all organic materials. In the case of a calamitic liquid crystal the intermolecular forces holding the molecules together in the crystal lattice are anisotropic, that is to say, they are not equal in all directions. The forces along the long molecular axis are larger in magnitude than those perpendicular to it, so the forces holding the molecules end to end break down first, resulting in a phase with partial loss of positional and orientational order intermediate between the crystalline solid state and the isotropic liquid. This phase is called a mesophase, the compounds exhibiting these are mesogens. Mesogens are termed liquid crystals because the mesophase behaves as both a liquid, because of its fluidity and as a crystal, as it retains some degree of order.

1.1.2 The Mesophases

Three possible mesophases can be exhibited by calamitic liquid crystals, depending upon the structure of the mesophase and whether the mesogen is chiral. These mesophases are called smectic, nematic and chiral nematic. Some phases are monotropic, that is they only appear on cooling. A more detailed account of these mesophases is given elsewhere [3,4,5].

1.1.2.1 Smectic/Crystal Phase

Smectic liquid crystals are viscous and opaque in appearance. This phase arises on heating a crystal lattice, when the inter-molecular forces between the layers break down before the forces between molecules within the layers, causing loss of long range positional and some orientational order. This results in a lamellar structure due to the fact that the layers remain more or less intact. In the smectic phase the layers are free to move over one another and molecules can move from one layer to another, so the phase is free to flow. Up to the present date, five smectic phases have been identified (SmA, SmB, SmC, SmF and SmI) and have little or no positional order between layers.

The phases (crystal B, E, G, H, J and K) possess long range positional order and layer flow does not occur, hence the term crystal phases. Note that there are two B phases, both with hexagonal packing of the molecules. The remaining phase, D possesses a cubic, not lamellar structure.

The main structural differences between the different phases are whether correlation is present or not between layers and the arrangements of molecules within the layers. These differences will be highlighted by considering the structures of SmA, SmB, SmC and crystal B (see figure **5.1**).

In the SmA phase, the least ordered smectic phase, there is no ordering of the molecules within the layers and no positional ordering from one layer to the next. The layers are not very clearly defined but all the molecules are perpendicular with respect to the layer plane and the phase can be considered to possess one-dimensional order.

In the SmB phase there is a regular hexagonal ordering of molecules within layers but there is still no positional ordering from one layer to the next. This phase can be considered to possess two-dimensional order.

In the crystal B phase there is positional ordering between molecules in the layers and from one layer to the next. This gives the phase three-dimensional order. This molecular correlation between layers can extend for hundreds or even thousands of layers but the range of this molecular correlation is not as extensive or as perfect as that found in true crystals and for this reason the crystal phases can be regarded as 'soft' crystals.

The phases described above all have the long molecular axes perpendicular to the layer planes. Some smectic phases, like SmC, have the molecular axes tilted with respect to the layer plane. The SmC phase can be regarded as a tilted version of SmA as there is no positional ordering within or between layers.

1.1.2.2 The Nematic Phase

This phase is much more fluid than the smectic/crystal phases as it does not possess a lamellar structure. It is much more akin to the isotropic liquid, the only ordering present is that the long molecular axes are statistically parallel to a preferred direction called the Director (n). Unlike the many different smectic phases that exist, there is only one nematic phase (see figure **5.2**).

1.1.2.3 Chiral Nematic Phase

This phase is simply the nematic phase displayed by chiral mesogens, for each slice made through the structure the long molecular axes all remain parallel to the local director. However the difference is that the director rotates about the optical axis

producing a helical structure. The helix can be either left or right handed, depending on the direction of optical rotation of the mesogen (see figure **5.3**).

The distance that the helix takes to rotate through 360° is called the pitch length (p). The wavelength of light (λ) reflected by the chiral nematic phase of refractive index (n) is given by equation **1.1**.

$$\lambda = np \qquad \text{Equation } \mathbf{1.1}$$

If the product np falls in the visible portion of the electromagnetic spectrum, coloured light will be reflected. As the pitch length is dependent upon temperature, then so must the colour of the reflected light, with red light being reflected at low temperatures and blue light at high temperatures. This enables chiral nematic liquid crystals to be used in devices designed to show temperature.

Mesogens containing a chiral centre can sometimes form smectic phases and indeed chiral versions of SmA, SmC, SmF and SmI are known. The chiral SmC phase (SmC*) will be discussed in more detail later.

1.1.3 Alignment

Liquid crystals can be aligned with respect to a surface in two different ways. These can be produced by the application of different alignment layers to the surface depending upon the type required. Homogeneous alignment can be produced by applying a thin layer of polymer, for example polyvinyl alcohol, polyimide or nylon-66, to the surface and rubbing it in one direction. This will cause the mesogens to lie parallel to the surface. Homeotropic alignment can be induced by treating the glass support surfaces with a surface active agent such as lecithin or a long chain

trichlorosilane such as n-octyltrichlorosilane, which will cause the mesogens to lie at right angles to the surface.

1.1.4 Anisotropic Properties

Liquid crystal phases possess optical anisotropy or birefringence (Δn), which, when light passes through the medium gives rise to double refraction. Liquid crystals therefore have two refractive indices. For a nematic phase they are given by equation **1.2**:

$$\Delta n = n_{\parallel} - n_{\perp} \qquad \text{Equation } \mathbf{1.2}$$

where $n_{\parallel}$ and $n_{\perp}$ are, respectively, the refractive indices parallel and perpendicular to the director.

The dielectric permitivity of liquid crystals is also anisotropic. This is the dielectric anisotropy, $\Delta\varepsilon$ and it is given by equation **1.3**:

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \qquad \text{Eqution } \mathbf{1.3}$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are, respectively, the dielectric permitivities parallel and perpendicular to the nematic director. Under the application of an electric field, in the absence of any other constraints, the director will align parallel to the field for material exhibiting positive $\Delta\varepsilon$ and perpendicular to the field for materials exhibiting negative $\Delta\varepsilon$.

1.1.5 Display Devices

The two properties of birefringence and dielectric anisotropy, along with the correct alignment, can be put to use in the production of display devices. For a more detailed account of liquid crystal display devices see elsewhere [6].

1.1.5.1 The Twisted Nematic Display Device

The twisted nematic (TN) display device is the most widely used type of liquid crystal display. The operation of the device is shown in figure **5.4**.

The device consists of two glass plates, which are made to function as electrodes by the application of a thin, transparent conducting layer of indium-tin oxide (ITO) on their inner surface. The ITO layer is etched with the appropriate pattern to display the characters required. The inner surface of the electrodes is also treated with an alignment layer to bring about a homogeneous alignment of the thin sample (6-10 μm) of nematic liquid crystal material which is held between the electrodes. The configuration of the electrodes is adjusted so as to induce a 90° twist of the director through the sample. Polarisers are attached to the outside of the electrodes with the direction of polarisation lying parallel to the surface director, that is, the polarisers are set at right angles to one another.

As light enters the top of the cell it is polarised in the direction of the director, as it passes through the cell it is rotated through 90° so that its direction of polarisation is parallel to that of the bottom polariser. Light is transmitted through the cell in this 'off state' and hence it appears bright. However, if an electric potential is applied across the cell, the macroscopic director re-orientates with respect to the resulting field and so the 90° twist is lost and the liquid crystal can no longer operate as a wave guide. Light is no longer transmitted by the cell, as its direction of polarisation is now

perpendicular to that of the bottom polariser and in this 'on state', the display appears dark. When the applied electric potential is removed, the molecules assume their original alignment because those at the electrode surfaces are so tightly bound that they are unaffected by the application of the electric field and this can act as a guide for the re-alignment of the bulk of the material.

1.1.5.2 Supertwisted Nematic Display Device

Despite its popularity, the TN display device suffers from some drawbacks; the response times are too slow for video frame rate switching, it also has a small viewing angle and the lack of 'memory' limits the size of the device. To overcome these problems the supertwisted nematic (STN) display device was developed. This display device is essentially the same as the TN device, the main difference being that instead of a twist of the director of 90° through the sample, the twist varies between 180° and 270°, depending upon the manufacturer. One of the alignment layers is also at an angle to the electrode surface.

Many variants of the STN display device are known but it is beyond the scope of this thesis to discuss these variations.

1.1.5.3 Ferroelectric Display Device

Ferroelectricity is exhibited by the SmC* phase. If the molecules forming the SmC* phase possess a lateral dipole which lies parallel to the layer planes but perpendicular to the tilt plane then the phase is ferroelectric. Passing through the layers of a SmC* sample it is found that the layers form a helical structure and that the dipoles average out to zero (figure **5.5**). However, if the helix is unwound, the dipoles will all point in the same direction and a permanent dipole will result and the phase becomes

ferroelectric. This formation of a permanent dipole is called spontaneous polarisation (Ps).

The application of an electric field to the ferroelectric phase causes the lateral dipole of the molecules to align with the field and in doing so the molecule moves round the surface of a cone, through an angle 2θ, where θ is the tilt angle of the SmC* phase (figure **5.5**). Due to the fact that the Ps couples directly with the electric field and that gyration round a cone is a natural mode of movement for molecules in the SmC* phase, the molecules can be switched between up and down states very rapidly which would enable a display device based on the ferroelectric phase to run easily at video frame rates. The ferroelectric phase is said to be bistable, because it can exist with the lateral dipoles of the molecule either in the up or down states, depending upon the direction of the electric field and the molecular dipoles.

In the ferroelectric display device (see figure **5.6**) the liquid crystal is placed homogeneously between the polariser and the analyser, with the director lying parallel with the surface and the layer planes lying perpendicular to the surface. In the 'off' state the molecules have their dipoles pointing upwards with the director parallel to the analyser but perpendicular to the to the polariser. Under these conditions no light is transmitted and the device appears dark. On application of an electric field the molecules move so that their dipoles are pointing down. If θ is equal to 22.5° then the director is now at angle of 45° to both the analyser and the polariser, so light can be transmitted and the device appears bright.

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1.2 An Introduction to Polymers

Polymers have been synthesised and studied for many years and their properties have been characterised [1]. A polymer is a macromolecule based on a number of repeat units which can be found in various systems, including linear or three dimensional forms.

1.2.1 Molecular Weight of a Polymer Sample

A sample of polymer is not a pure compound in the usual sense, even if pure monomer is used and the polymer is synthesised without incorporation of impurities. This is because a sample of polymer consists of molecules with a range of molecular weights. Since a distribution of weights is present, the average molecular weight and the molecular weight distribution are both required to fully characterise the sample. Various methods can be used to obtain the molecular weight of a polymer sample as described below.

1.2.1.1 Number Average Molecular Weight

The number average molecular weight ($\overline{M}_n$) is determined experimentally by methods which count the number of molecules in a sample. Methods suitable are those which measure the colligative properties of polymer solutions, for example, vapour pressure osmometry and membrane osmometry. The $\overline{M}_n$ is defined as the

total weight of the molecules in a sample divided by the total number of molecules and is given by the following equation

$$\overline{M}_n = \Sigma N_x M_x \qquad \text{Equation 1.2.1}$$

from x = 1 to ∞ where N_x is the number fraction of molecules whose molecular weight is M_x.

For polymers with molecular weights of less than twenty thousand to thirty thousand end group analysis by a suitable method, for example, ^{1}H NMR can be used to obtain $\overline{M}_n$.

Once the $\overline{M}_n$ has been determined the average number of repeat units per polymer molecule can be calculated. This is referred to as the degree of polymerisation (DP) and is described by the equation:

$$DP = \overline{M}_n/Mr \qquad \text{Equation 1.2.2}$$

where Mr is the relative molecular weight of the monomer.

1.2.1.2 Weight Average Molecular Weight

The weight average molecular weight ($\overline{M}_w$) is determined experimentally by light scattering techniques on polymer solutions. Unlike colligative properties, light

scattering is greater for larger sized molecules than for smaller ones, hence the $\overline{M}_w$ is biased towards the larger end of the weight distribution. The $\overline{M}_w$ is defined as:

$$\overline{M}_w = \Sigma\, w_x\, M_x \qquad \text{Equation } \mathbf{1.2.3}$$

where w_x is the weight fraction of molecules whose weight is M_x.

1.2.2.1 Molecular weight distribution

As already mentioned a sample of polymer consists of molecules of different molecular weight. It is desirable to know what the spread of molecular weight is. Since $\overline{M}_w$ is always larger than $\overline{M}_n$ for the same sample then a useful measure of the weight distribution called the polydispersity (PDI), which is given by:

$$\text{PDI} = \overline{M}_w / \overline{M}_n \qquad \text{Equation } \mathbf{1.2.4}$$

1.2.2.2 Measuring Molecular Weight Distribution

It is often necessary to obtain the exact distribution of molecular weight. The most common method for this is the use of size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC). In this procedure a sample of polymer is passed through a porous column made up of beads of cross-linked polystyrene. The beads incorporate a range of pore sizes so that a wide molecular weight range can be separated by the technique.

Molecules progress through the column by a combination of passing through the interstitial volume (the volume between the beads) and passing into and through the pores within the beads. Molecules travel more quickly through the interstitial volume but more slowly through the pores. The smaller the polymer molecules, the more pores they can penetrate, therefore the slower they are eluted through the column. The larger the molecules, the less pores they can penetrate, therefore they spend more time in the interstitial volume and are eluted more quickly.

The time for elution of a polymer molecule is inversely proportional to the *log* of the molecular weight, so with the use of an appropriate detector (e.g. refractive index) the amount of polymer coming off the column can be obtained as a function of time. If the column has been calibrated with standards of known molecular weight then the $\overline{M}_n$ and $\overline{M}_w$ of the sample can be calculated.

1.2.3.1 Physical State of Polymers

When considering the physical state or morphology of polymers in the solid state they differ from low molecular weight compounds in that most polymers simultaneously show characteristics of both crystalline solids and highly viscous liquids. The crystalline regions of the polymer are highly ordered and the amorphous regions are disordered. The complete range of morphology is displayed by known polymers, ranging from completely amorphous through to highly crystalline materials. A completely crystalline polymer sample is very uncommon.

1.2.3.2 Thermal Transitions of Polymers

Polymers possess two major thermal transitions, the crystalline melting temperature (Tm) and the glass transition temperature (Tg). The Tm is the temperature at which the crystalline domains of the polymer sample melt. The Tg is the temperature at which the amorphous domains of the sample become glassy, that is to say stiff, brittle and rigid.

To describe the difference between the Tm and the Tg consider the changes occurring to a liquid polymer as it cools. On cooling, the translational, rotational and vibrational energies decrease. When the polymer is sufficiently cooled, these energies will be low, so that crystallisation is possible. If the symmetry of the system is such that the molecules can pack into a crystal lattice, then crystallisation will occur at the Tm. If the symmetry requirements for crystallisation cannot be met, then crystallisation will not take place. On further cooling, the Tg is reached and at this point all long range motions of the polymer chains stop. However, if the polymer contains side chains, then rotations of these groups about the bonds attaching them to the polymer chain does not cease at the Tg.

The morphology of a polymer sample determines whether the polymer exhibits a Tm, Tg or both. If a polymer is completely crystalline then it will only display a Tm. If it is semi-crystalline then it will exhibit both Tm and Tg. If it is completely amorphous then it will only exhibit a Tg.

The most common method for the determination of these thermal transitions is differential scanning calorimetry (DSC). The use of DSC will be discussed later.

1.2.4 Reference

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1.3 Introduction to Liquid Crystal Polymers

There was little interest shown in the liquid crystalline properties of polymers until, in the 1950's, it was found that a film of a solution of the polypeptide poly(-benzyl-L-glutamate) showed birefringence [1]. A more thorough investigation was conducted and it was found that the polypeptide showed liquid crystal properties very similar to those exhibited by low molar mass materials. Previously, polymer scientists had only investigated the amorphous and crystalline states of polymers. However, it was not until much later that a systematic study of the synthesis and properties of liquid crystal polymers was undertaken.

There are two main types, main chain liquid crystal (MCLC) polymers and side chain liquid crystal (SCLC) polymers.

1.3.1 Main Chain Liquid Crystal Polymers

Main chain liquid crystal (MCLC) polymers incorporate the mesogenic unit directly into the main chain of the polymer backbone. These types of polymer can either be rigid, with the mesogenic side groups directly attached to the polymer backbone, or they can be semi-rigid, where there is a flexible spacer between each mesogenic group and the backbone, as shown in figure **1.3.1**.

Rigid backbone:

Flexible backbone:

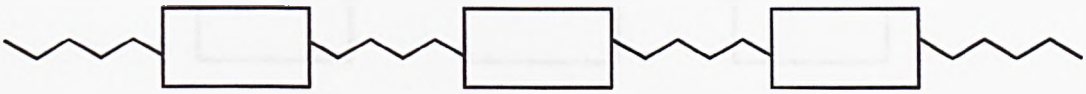


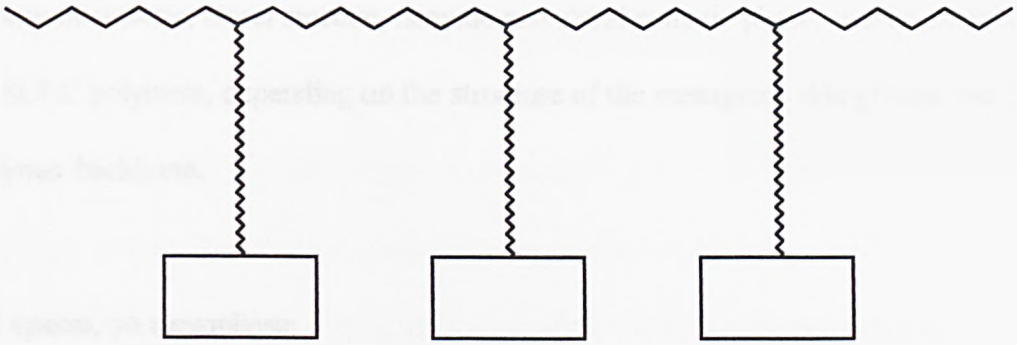
Figure **1.3.1**

Rigid (MCLC) polymers tend to be insoluble in most organic solvents and also tend to decompose on heating before exhibiting liquid crystalline phases. Therefore, it is only the semi-rigid polymers that have useful applications, especially as high tensile strength materials [2]. These materials will not be discussed any further.

1.3.2 Side Chain Liquid Crystal Polymers

These polymers result when the mesogenic side group is attached to the polymer backbone, like teeth on a comb, rather than being structurally combined within it. The mesogenic side groups can be appended as side chains from the backbone in two ways; laterally and terminally as shown in figure **1.3.2.**

Lateral attachment:



Terminal attachment:

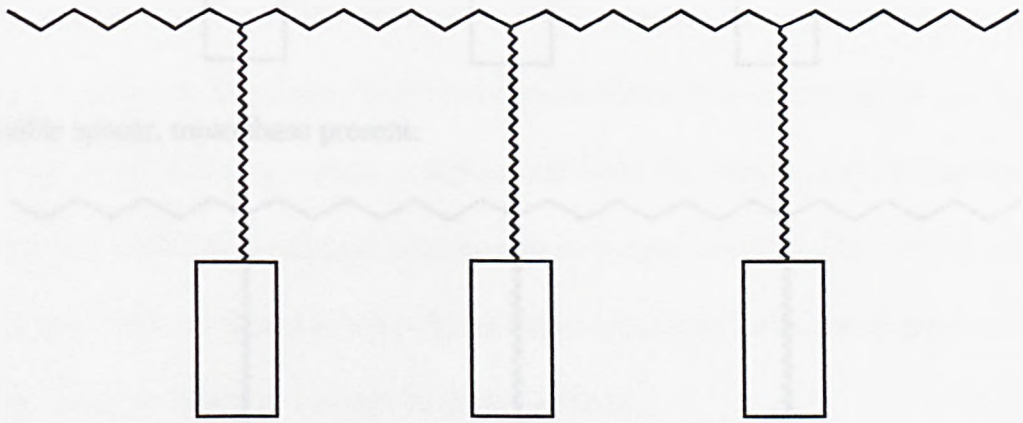


Figure **1.3.2**

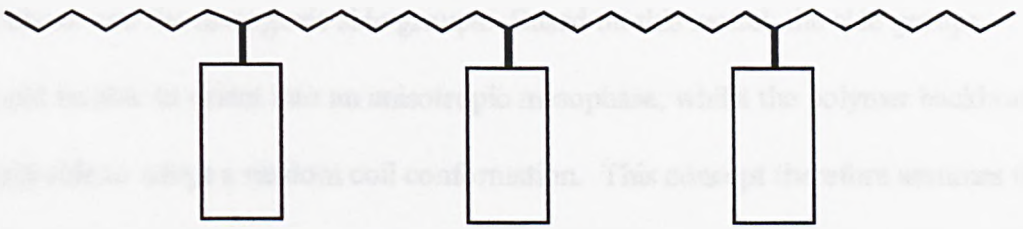
1.3.2.1 An Introduction to Side Chain Liquid Crystal Polymers

This introduction will only deal with thermotropic SCLC polymers based on rigid rod-like mesogens which exhibit calamitic phases.

If the mesogenic side groups are attached directly to the polymer backbone it is found that such polymers do not produce mesophases. However, work has been carried out which showed that if a flexible spacer is inserted between the polymer backbone and

the mesogenic side group then a mesophase should result [3] (see figure **1.3.3**). A variety of smectic, chiral smectic, nematic and chiral nematic phases can be exhibited by SCLC polymers, depending on the structure of the mesogenic side groups and the polymer backbone.

No spacer, no mesophase:



Flexible spacer, mesophase present:

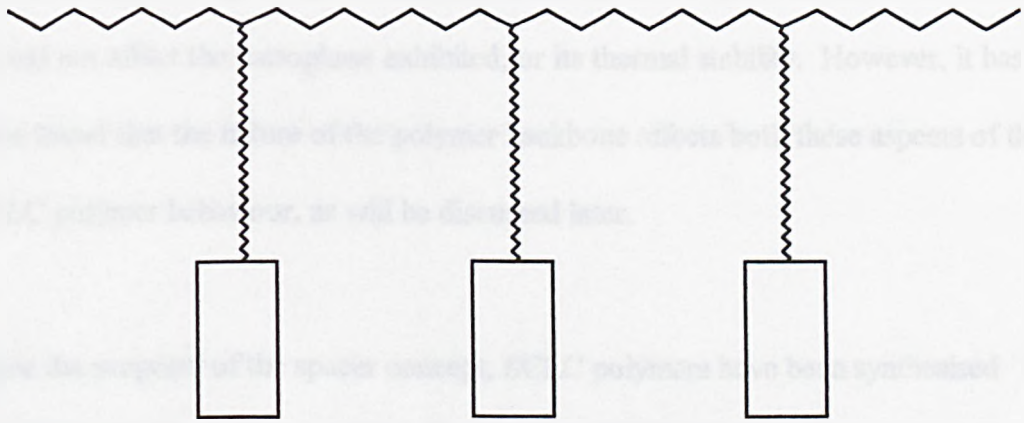


Figure **1.3.3**

1.3.2.2 Partial Decoupling By Spacer

When mesogenic side groups are directly attached to the polymer backbone, it is accepted that the motions of the main chain and side group are coupled. This means that formation of a mesophase is not likely to occur because there is competition between the flexible main chain, which tends to form a statistically random coil, and

the mesogenic side groups, which tend to arrange anisotropically [4].

In order to balance the backbone's random coil conformation and the anisotropic nature of the mesogenic side groups, it was predicted that the motions of the main chain and side groups be decoupled from one another in the fluid state [5,6]. Decoupling can be achieved by inserting a flexible spacer group between the polymer backbone and the mesogenic side groups. Based on this model, the side groups should be able to orient into an anisotropic mesophase, whilst the polymer backbone is still able to adopt a random coil conformation. This concept therefore assumes that the main chain will have little effect on the orientation of the mesogenic side groups. That is to say, for a given spacer group and mesogen, the type of polymer backbone should not affect the mesophase exhibited, or its thermal stability. However, it has been found that the nature of the polymer backbone affects both these aspects of the SCLC polymer behaviour, as will be discussed later.

Since the proposal of the spacer concept, SCLC polymers have been synthesised routinely by many research groups. It has been demonstrated that a spacer group helps to decouple, or partially decouple, the motions of the mesogenic side groups from the polymer backbone. This decoupling effect increases with increasing length of spacer group. However, decoupling is incomplete, with at least part of the spacer group being anisotropically oriented with the mesogen. The most accurate way to visualise a SCLC polymer is the interaction of two semi-independent thermodynamic subsystems *via* the flexible spacer group, with a section of the spacer plasticising the polymer chain, while another section stabilises the mesogenic side groups [4,7,8].

Additional support for only partial decoupling comes from the fact that below the glass transition (Tg) the motions of the mesogenic side groups are frozen, except for 180° rotations of the benzene rings about the long molecular axis of the mesogen [9].

In certain SCLC polymeric systems, especially those based on a very flexible polymer backbone, for example polysiloxanes, it is possible for microphase separation to occur. In such systems the polymer backbone and the mesogenic side groups exist in discrete domains within the polymer preparation. If this is so, the system will show two glass transition temperatures, one corresponding to the polymer backbone and the other corresponding to the motions of the side chains [10-14]. Under these conditions the mesogen is completely decoupled from the backbone.

1.3.2.3 Influence of the Polymer Backbone and Spacer Length On Thermal Transitions

With increasing flexibility of the polymer backbone there is an increase in the thermal stability of the mesophase and also a trend towards higher isotropisation temperatures [15].

The isotropisation temperature is affected by the spacer length. For a given polymer backbone and mesogen; after an initial decrease, the isotropisation temperature increases with increasing length of the spacer group.
The T_g is also affected, it decreases with both increasing backbone flexibility and increasing spacer length.

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1.4 An Introduction to Polymerisation

Polymers can be produced by three different methods, step growth polymerisation, polymer modification reactions and chain growth polymerisation [1,2].

1.4.1 Step Growth Polymerisation

Step polymerisation occurs between two different bifunctional and/or polyfunctional monomers. Usually each step in the polymerisation proceeds with the elimination of a small molecule e.g. water, hence the alternative term, condensation polymerisation. Polymerisations of this type fall into two classes, as can be illustrated by the following two different polyesterifications.

The first type involves monomers which only possess one type of functional group, for example, the polymerisation of ethylene glycol and terephthalic acid, as shown in figure **1.4.1**.

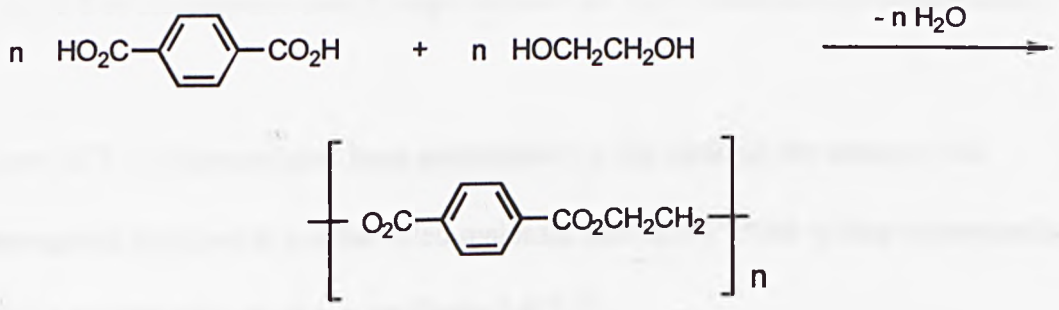


Figure **1.4.1**

The second type involves monomers which possess both types of functional group required for the reaction, for example the polymerisation of p-hydroxybenzoic acid, as shown in figure **1.4.2**.

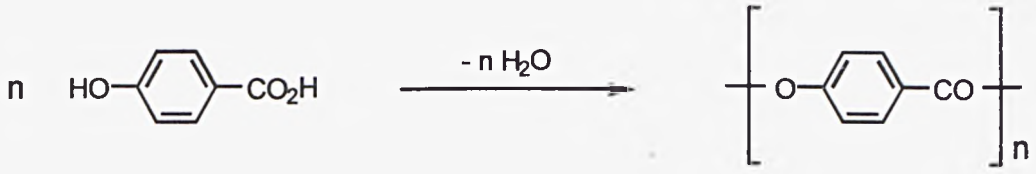


Figure **1.4.2**

Other types of polymer which fall under this general heading include polyamides, polysiloxanes, polycarbonates and polyurethanes.

The polymerisation reaction proceeds by the addition of two monomers to give a dimer. Then two dimers can combine to give a tetramer or a dimer can add one monomer molecule to form a trimer. The reaction proceeds in this manner, with the rapid removal of monomer from the system and the formation of low molecular weight polymer. High weight polymer is only obtained with very high conversion. The PDI of the polymer usually approaches 2 for high conversion polymerisations.

Some SCLC polymers have been synthesised by this method, for example the mesogen is attached to a substituted malonate derivative which is then transesterified with a suitable diol, as shown by figure **1.4.3** [3,4].

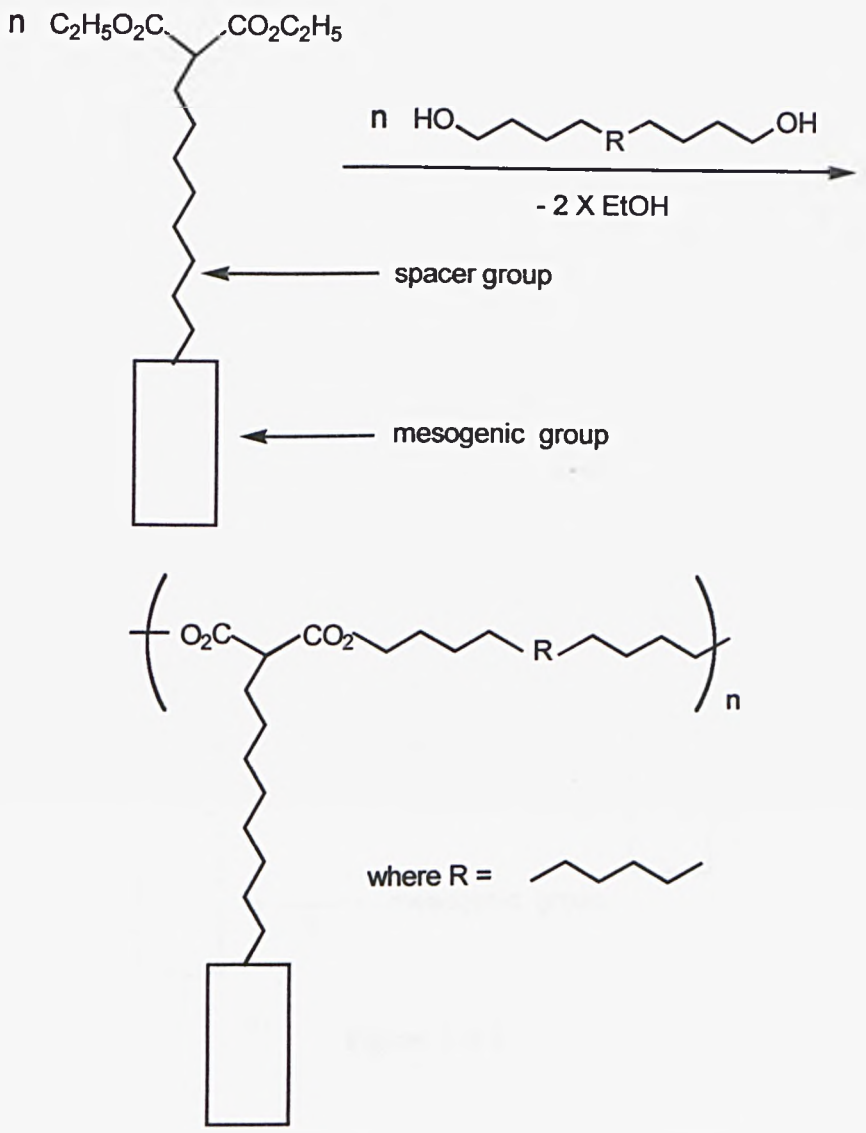


Figure **1.4.3**

1.4.2 Polymer Modification Reactions

This method of polymer production involves modification of an already synthesised polymer backbone, utilising the presence of unreacted groups along the polymer backbone, for example the hydrosilylation reaction. This involves the addition of a mesogen and flexible spacer, containing a terminal alkene, to a suitable polysiloxane

backbone, for example poly(hydrogen methyl)siloxane. The reaction is catalysed by complexes of platinum, such as hexachloroplatinic acid, as shown in figure **1.4.4** [5].

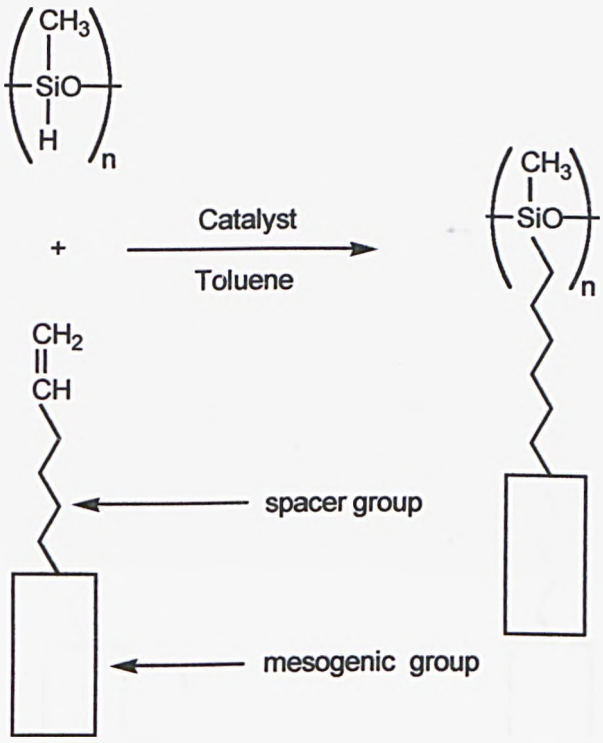


Figure **1.4.4**

1.4.3 Chain Growth Polymerisation

This type of reaction usually involves attack at a carbon-carbon double bond. The reaction can be initiated by either a free radical, cationic or anionic initiators. The PDI value for the polymers also approaches 2 for polymerisations of this type However, in the case of the ionic mechanisms if the initiation and propagation reactions are fast in relation to termination reactions, then the PDI value may only be just greater than 1.

The mesogen and spacer groups are usually already present in the monomer before polymerisation occurs. For example, SCLC polymers can be synthesised by free radical polymerisation of acrylic acid derivatives, as shown in figure **1.4.4** [6].

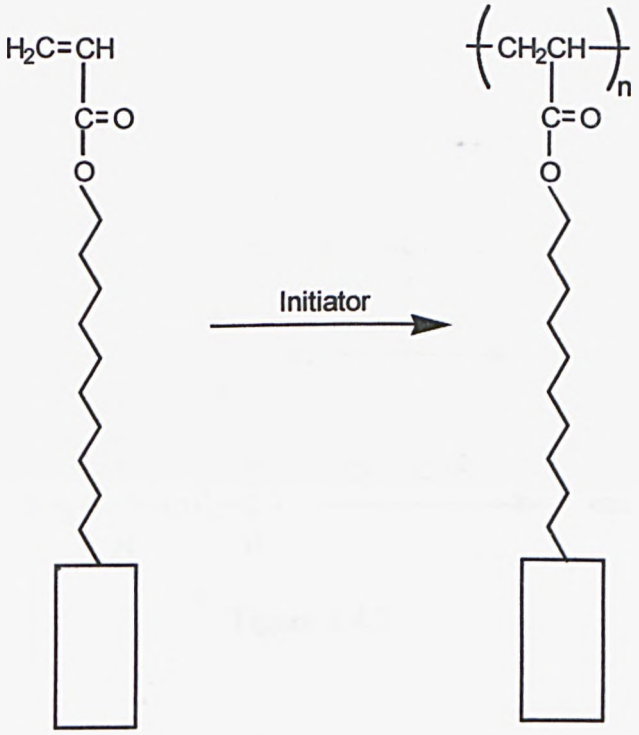


Figure **1.4.5**

Chain growth polymerisation can be split into three distinct processes, initiation, propagation and termination.

1.4.3.1 Initiation

This process involves the formation of an active centre, either a cationic, anionic or radical species, usually by the addition of an initiator (figure **1.4.6**).

Figure **1.4.6**

1.4.3.2 Propagation

This process involves a sequence of steps by which the polymer chain grows by the active centre adding successive monomer molecules (Figure **1.4.7**).

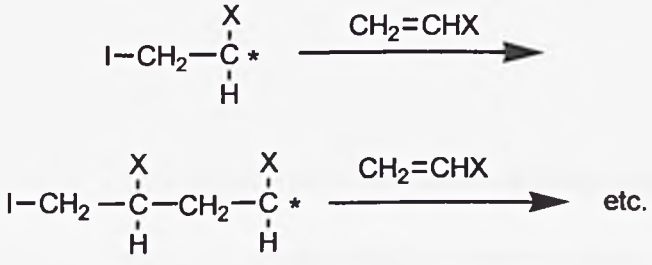


Figure **1.4.7**

1.4.3.3 Termination

This process involves destruction of the active centre by combination with another species present, or transferal of the reactive centre to another species which does not result in further polymerisation.

1.4.4 Cationic Polymerisation

Cationic polymerisation occurs in alkenes with electron releasing substituents e.g. styrene, vinyl ethers etc [7]. The initiator can be a protic acid, the anion of which is not nucleophilic e.g. perchloric acid (figure **1.4.8**).

Figure **1.4.8**

The initiator can also be a Lewis acid, the most important being aluminium chloride, when combined with a protogen (a species which provides a proton e.g. water, hydrogen halide or carboxylic acid) (figure **1.4.9**) or a cationogen (a species which provides a carbocation e.g. t-butyl chloride) (figure **1.4.10**). The protogen or cationogen is known as the initiator and the Lewis acid is known as the coinitiator. Together they react to form an initiator-coinitiator complex, which brings about addition of a reactive centre to a monomer molecule and initiates propagation.

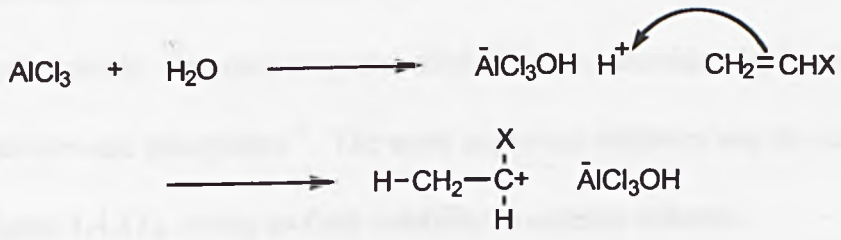


Figure **1.4.9**

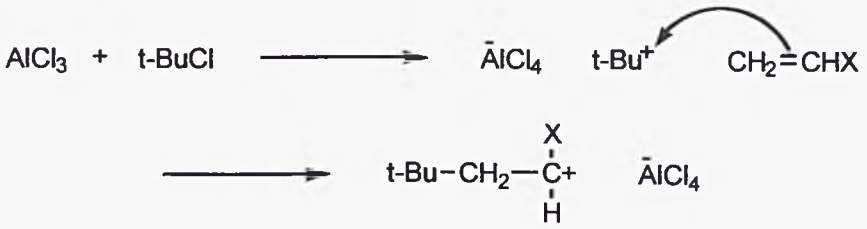


Figure **1.4.10**

The propagating species does not consist of free ions but as an ion pair. Termination can occur by processes such as reaction of the active centre with impurities , by the addition of terminating agents, combination with counterion or spontaneous termination. The first three are both self explanatory but spontaneous termination occurs when the original initiator species is regenerated, leaving the polymer chain with terminal unsaturation.

1.4.5 Anionic Polymerisation

Anionic polymerisation can occur with monomers bearing electron withdrawing groups e.g. acrylates, methacrylates and acrylonitrile. Essentially, the initiator must be nucleophilic and not necessarily anionic, however a carbanion is involved in the propagation step. Examples of initiators include metal amides e.g. sodamide and lithium di-ethyl amide, Grignard reagents, alkyl lithiums, alkoxides, hydroxides, cyanides, amines and phosphines [8]. The most important initiators are the alkyl lithiums (figure **1.4.11**), owing to their solubility in organic solvents.

Figure **1.4.11**

When the initiator is neutral, as in the case for amines and phosphines (figure **1.4.12**), the propagating species is zwitterionic.

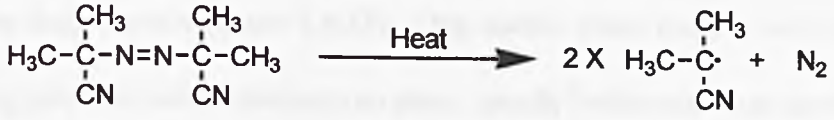
Figure **1.4.12**

Apart from the above example, propagation usually involves an ion pair, similar to that found in cationic polymerisation and termination can occur by reaction with impurities or the deliberate addition of terminating agents. However, combination with the counter ion is rare and if the reagents used are very pure, termination does not occur. This results in what is known as a living polymerisation (see later).

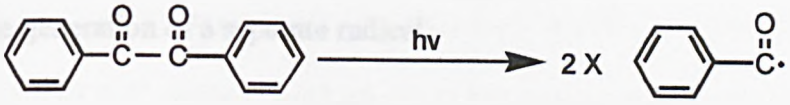
1.4.6 Free Radical Polymerisation

Free radical polymerisation of the carbon-carbon double bond can occur for alkenes bearing a wide variety of functional groups (see later) [2]. Polymerisation is initiated by a radical produced from the initiator, either by heat (thermal initiation) or light (photoinitiation). An example of a thermal initiator is azo-bis-isobutyronitrile

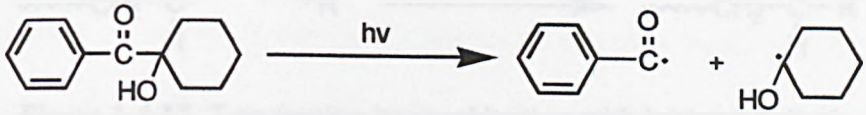
(AIBN). Examples of photoinitiators are benzil and Irgacure 184 (Ciba-Geigy), as shown in figure **1.4.13.**



Thermolysis of AIBN



Photolysis of benzil



Photolysis of Irgacure 184

Figure **1.4.13**

The radical adds to a monomer molecule by opening the π bond to form a new radical. Propagation simply consists of the addition of successive monomer molecules to the growing radical, as shown in figure **1.4.14.**

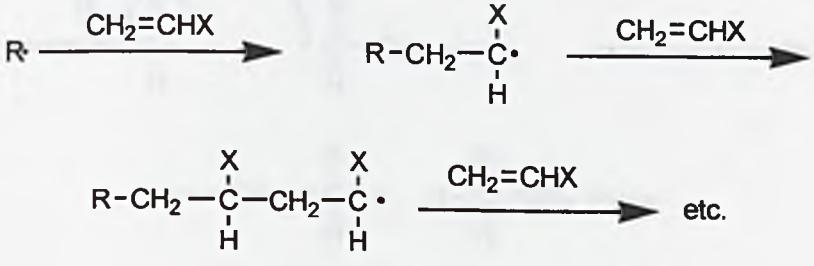


Figure **1.4.14**

At some point the reactive centre is destroyed or transferred to another species and the polymer chain stops growing. This can happen by combination with another radical (figure **1.4.15** and **1.4.16**), by disproportionation (figure **1.4.17**) or by degradative chain transfer (figure **1.4.18**). Degradative chain transfer occurs when the growing polymer radical abstracts an atom, usually hydrogen, from another species present in the reaction mixture, thus terminating the growth of the polymer chain and the generation of a separate radical.

Figure **1.4.15** Termination by combination with initiator radical.

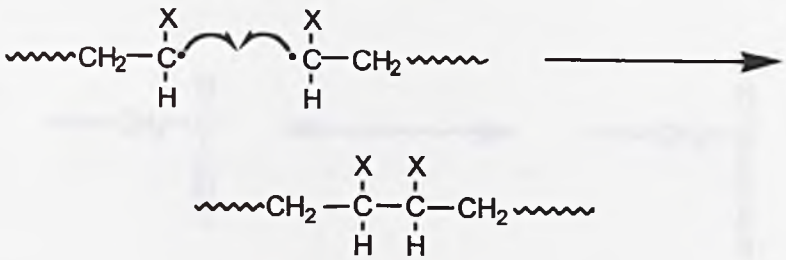


Figure **1.4.16** Termination by combination of two polymer chains.

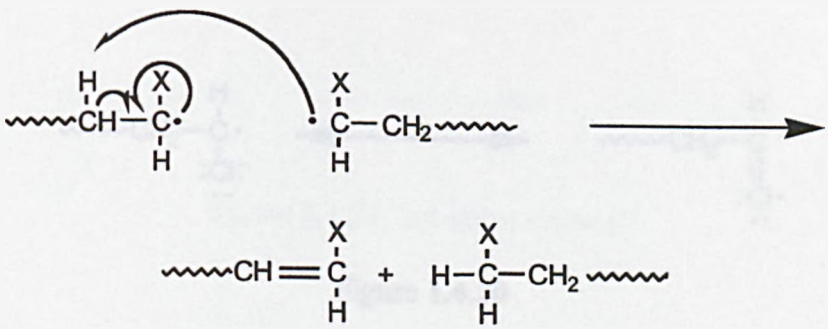


Figure **1.4.17**

Figure **1.4.18**

1.4.6.1 Effects of Substituents

Radical polymerisation reactions are not particularly sensitive to substituents, apart from 1,2-disubstituted alkenes which do not polymerise easily for steric reasons, as most radicals will easily add to most carbon-carbon double bonds bringing about polymerisation. However, a variety of substituents can stabilise the propagating radical by resonance effects. For example consider the polymerisation of acrylonitrile (figure **1.4.19**), vinyl chloride (figure **1.4.20**) and styrene (figure **1.4.21**).

Figure **1.4.19**

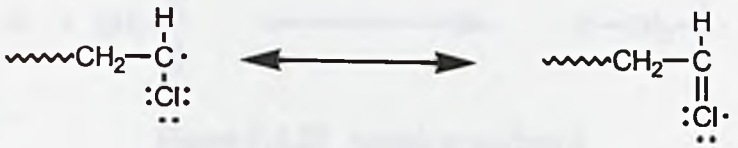


Figure **1.4.20**

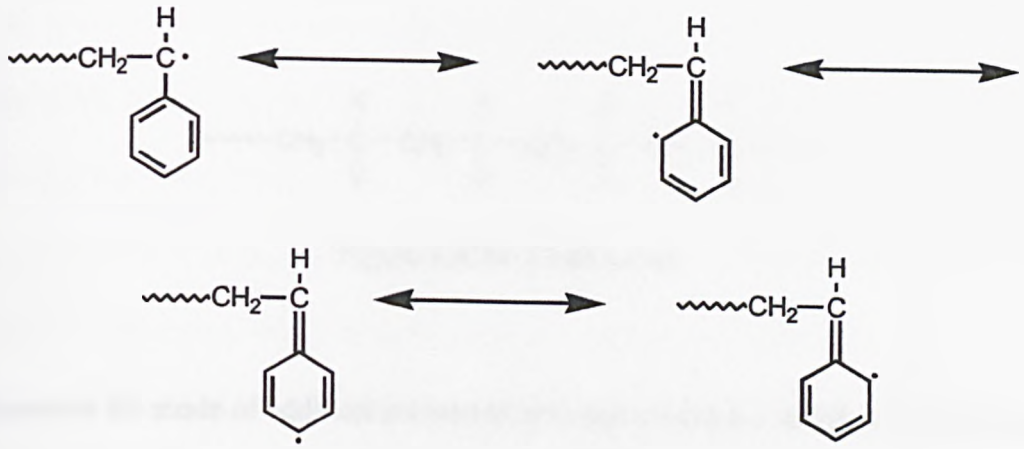


Figure **1.4.21**

1.4.6.2 Modes of Propagation

There are two possible points of attachment on 1-substituted alkenes, these being attack at carbon 1 or at carbon 2.

Figure **1.4.22** Attack at carbon 1

Figure **1.4.23** Attack at carbon 2

If each monomer molecule adds progressively to the propagating chain in the same manner then the substituents X and Y will be on alternate carbons. This is called a head to tail arrangement (figure **1.4.24**).

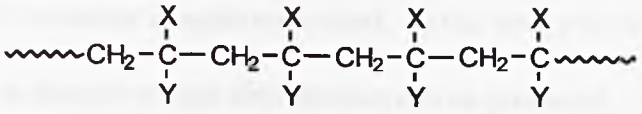


Figure **1.4.24** Head to tail

If however the mode of addition is inverted between successive additions of monomer molecules, a head to head arrangement is obtained (figure **1.4.25**).

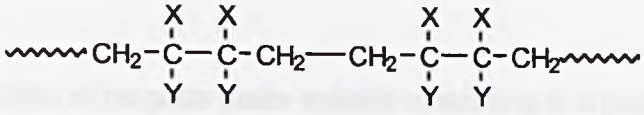


Figure **1.4.25** Head to head

It has been found by experiment that head to tail addition predominates and this can easily be understood, as attack at carbon 2 is favoured on both steric grounds and because the newly formed radical will be stabilised by the substituents X and Y on carbon 1.

1.4.7 Living Polymerisation

1.4.7.1 Anionic

As mentioned previously when considering anionic polymerisation, if all reagents are very pure, then termination does not occur. When all the monomer has been consumed each polymer molecule still has a reactive anionic centre present at one

end. If more monomer is introduced, then it adds to the polymer chains as before until all the added monomer is again consumed. In this way polymers of well defined and very narrow molecular weight distributions can be produced. Also, it is possible to produce block co-polymers by this process; once all the initial monomer has been used up a different monomer is added and once that has reacted the process can be repeated as required.

1.4.7.2 Cationic

With careful selection of reagents under suitable conditions it is possible to obtain living cationic polymerisation. It is necessary to use a reaction system with propagating centres of low reactivity, such that termination and transfer reactions do not occur but not so unreactive as to suppress propagation. An example of such a system is illustrated in figure **1.4.26** [9].

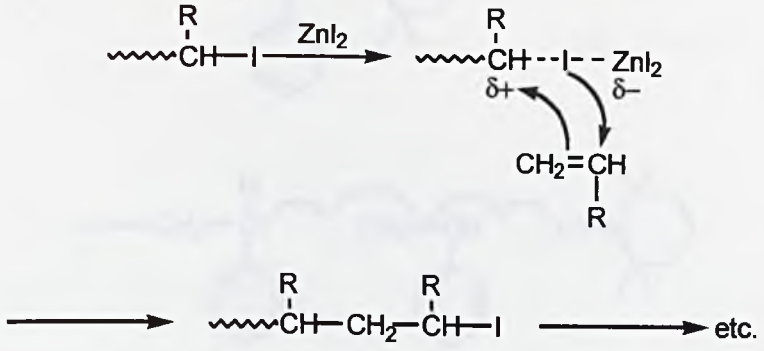
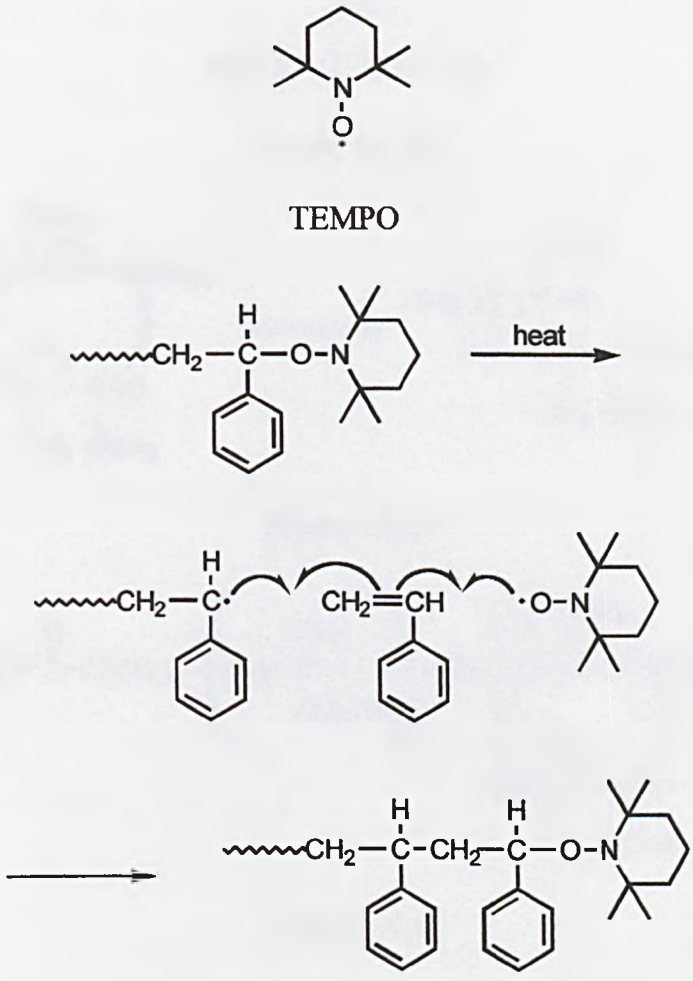


Figure **1.4.26**

1.4.7.3 Free Radical

Living polymerisation can be achieved by a radical mechanism if a suitable 'counter' radical is used. The counter radical is used in conjunction with the initiator, combining with the radical produced when the initiator adds to a molecule of monomer. Under the reaction conditions this 'counter' radical combines reversibly with the polymer radical so as to prevent termination or transfer reactions. An example of such a system is the polymerisation of styrene in the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) (figure **1.4.27**) [10].



TEMPO

Figure **1.4.27**

1.4.7.4 Group Transfer Polymerisation

To overcome some of the problems of living anionic polymerisation of acrylates and methacrylates, group transfer polymerisation (GTP) was devised [11]. The use of GTP avoids the need for low reaction temperatures. The initiator is a silyl ketene acetal (figure **1.4.28**) with the initiation step involving concerted addition of the initiator to a monomer molecule (figure **1.4.29**). This results in the transfer of the silyl ketene acetal centre to the monomer. Propagation is exactly the same, with the double bond of the silyl ketene acetal acting as the active centre (figure **1.4.30**).

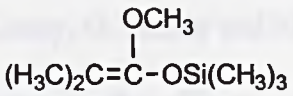


Figure **1.4.28**

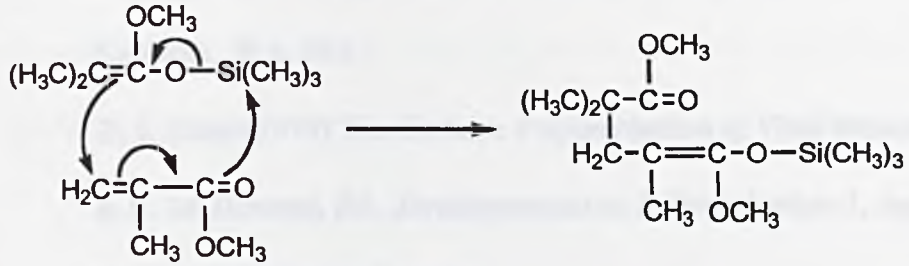


Figure **1.4.29**

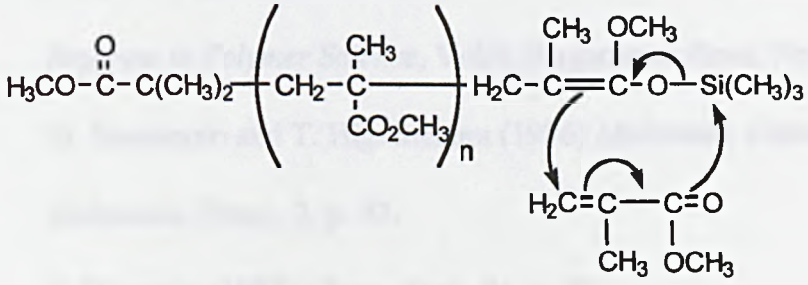


Figure **1.4.30**

1.4.8 References

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1.5 Introduction To Cyclopolymerisation

When non-conjugated diene monomers are polymerised it is possible for two different mechanisms to operate. The simplest of these would be 'normal' polymerisation where only one of the double bonds takes part in the polymerisation reaction. This mechanism would produce polymers with pendant unsaturation and the possibility of cross-linking. The other possibility would be *cyclopolymerisation* [1] which involves the alternating inter- and intra-molecular addition of the propagating radical, utilising both double bonds present in the monomer. This results in a linear polymer with no unsaturation or cross-linking. The choice between the two mechanisms is governed by the kinetic relationship between cyclopolymerisation and 'normal' propagation [2]. This relationship is shown in figures **1.5.1**, **1.5.2** and **1.5.3**. Figure **1.5.1** shows the 'normal' mechanism. Figures **1.5.2** and **1.5.3** show the two possible mechanisms by which cyclopolymerisation can operate depending on the structure of the diene and the size of the ring formed.

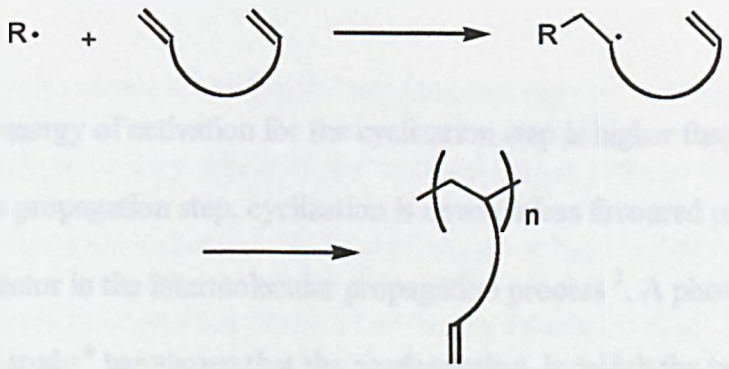


Figure **1.5.1**

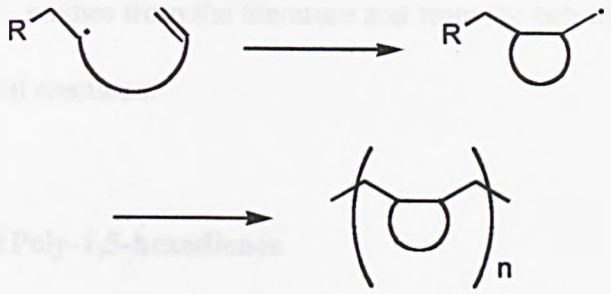


Figure **1.5.2**

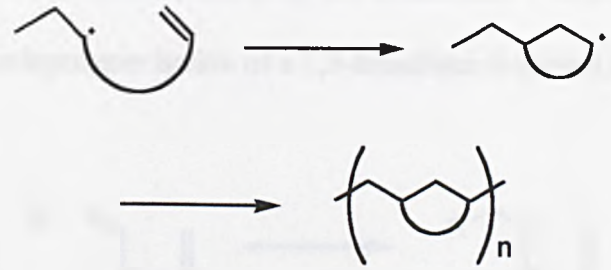


Figure **1.5.3**

In cyclopolymerisation an intramolecular cyclisation process occurs in the first step, cyclisation then occurs with the formation of a new radical which allows chain propagation to occur. This type of polymerization is often referred to as *intramolecular-intermolecular polymerisation.*

Although the energy of activation for the cyclization step is higher than that for the intermolecular propagation step, cyclization is nevertheless favoured probably due to a high steric factor in the intermolecular propagation process [3]. A photoelectron spectroscopic study [4] has shown that the conformation, in which the two double bonds of a 1,5-diene are crossed or in close proximity, is more stable by 9.6 kJ/mol than the open-chain conformation. Evidence to support the view that these polymer backbones are made up of repeating alicyclic-ring units comes from

IR [2] and ^{13}C NMR [3] studies from the literature and from the behaviour of analogous dienes in free radical reactions.

1.5.1 Ring Size of Poly-1,5-hexadienes

Degradation studies have also been performed in order to investigate the cyclic structures of poly-1,5-hexadienes and poly-1,6-hexadienes [5]. A possible structure produced by the cyclopolymerisation of a 1,5-hexadiene is shown in figure **1.5.4**.

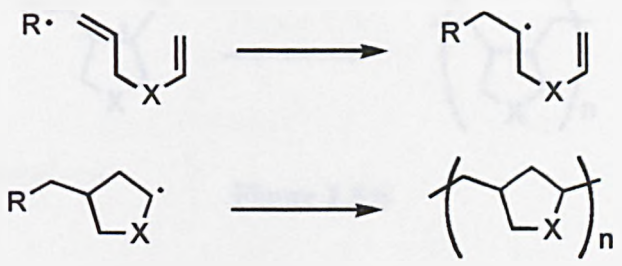


Figure **1.5.4**

1.5.2 Ring Size of Poly-1,6-heptadienes

The situation with respect to the formation of the free radicals in the synthesis of the poly-1,6-heptadienes is very similar to that outlined for the poly-1,5-hexadienes. However, the free radicals formed can now attack positions C-1 and C-2 to form a polymer backbone incorporating either a five- or six-membered ring. Cyclisation at C-1 to form a six membered ring is shown in figure **1.5.5** and cyclisation at C-2 to form a five membered ring is shown in figure **1.5.6**.

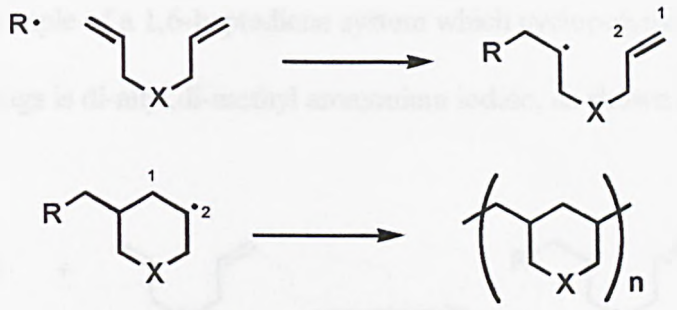


Figure **1.5.5**

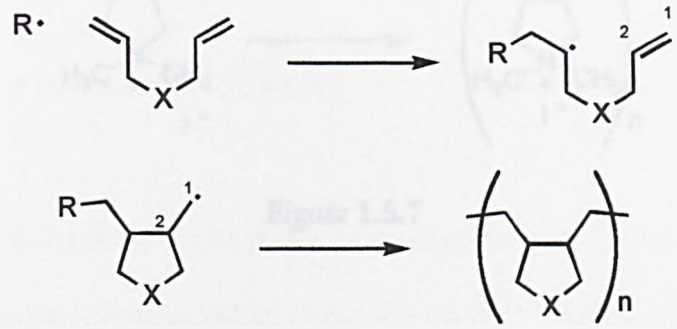


Figure **1.5.6**

The six-membered structure in figure **5** has been proposed based on the idea that in such free-radical polymerizations the more stable free radical would control the course of the polymerization [5]. However, later studies have shown that in numerous cases of cyclopolymerization the cyclic structure is derived by propagation through the less stable intermediate, i.e., the five-membered structure, and that such cyclopolymerizations are *kinetically* rather than thermodynamically controlled [4, 6-8]. Evidence for the preference of the kinetically controlled five-membered ring structure has been based on both electronic and steric considerations, suggesting interactions between the initially formed free radical and the neighbouring double bond of the diene. Such interactions lead preferably, to the formation of the five-membered ring

structure. An example of a 1,6-heptadiene system which cyclopolymerises to give five membered rings is di-allyl,di-methyl ammonium iodide, as shown in figure **1.5.7** [6].

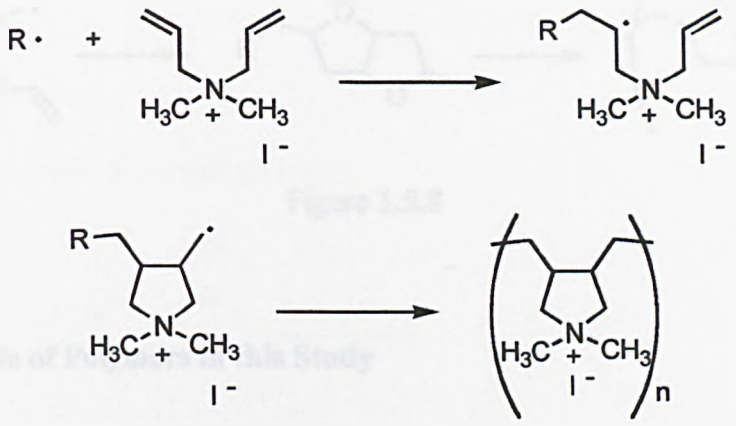


Figure **1.5.7**

1.5.3 Poly-1,4-pentadienes

A comprehensive study of the structures produced when 1,4-pentadienes are polymerized has also been made [9]. Polymerization of the 1,4-pentadiene monomers produces a very unusual structure which consists of (3,3,0) bicyclooctyl units separated by two methylene units as illustrated by the polymerisation of di-vinyl ether, as shown in figure **1.5.8**. This results from the radical which is initially formed, reacting in an intermolecular step with another monomer molecule, to form a second radical with the required structure for cyclopolymerisation to proceed.

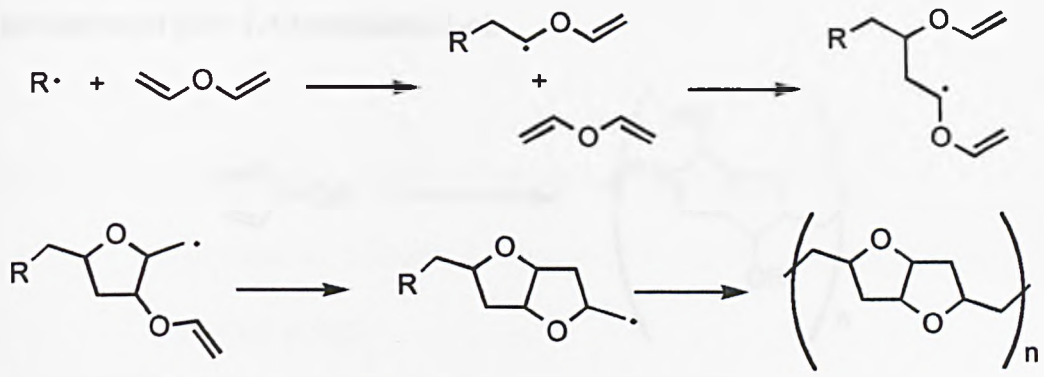
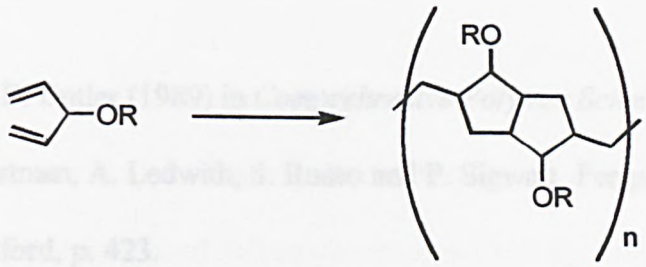


Figure **1.5.8**

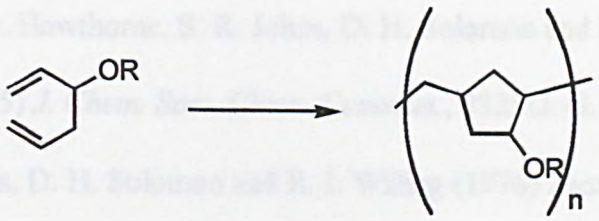
1.5.4 Structure of Polymers in this Study

In the work that is described in this thesis an assumption is made, based upon the ample evidence in the literature and from our own work [10] that the polymer backbones are as shown in figure **1.5.9**.

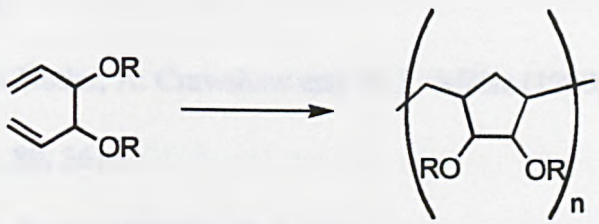
Derivatives of poly-1,4-pentadiene-3-ol:



Derivatives of poly-1,5-hexadiene-3-ol:



Derivatives of poly-1,5-hexadiene-3,4-diol:



Derivatives of poly-1,6-heptadiene-4-ol:

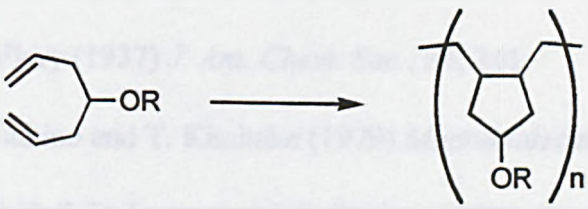


Figure **1.5.9**

1.5.5 References

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1.6 Aims of the Project

Most SCLC polymers rely on the more common types of polymer backbone; e.g. polymers of acrylate, methacrylate and siloxane derivatives. This project has involved the introduction of a new series of polymer backbones in the synthesis of SCLC polymers. This novel method involves the cyclopolymerisation of suitably substituted non-conjugated dienes to produce polymers incorporating alicyclic rings within the polymer backbone. The main advantage of this new methodology is that it has seldom been used to synthesise SCLC polymers in the past, so there is great scope for the production of new polymer systems.

The first main aim of this project was to optimise the polymerisation procedure, so as to maximise yields and optimise the molecular weight distribution. Once this had been done a programme of synthesis was undertaken to produce SCLC polymers which produced the SmC* phase, for use in display devices and for optical storage.

It was found with these new polydiene systems that some of the SCLC polymers produced wide SmC* phases, in the range ≈ 20 to 170 °C. Unfortunately, most of the SCLC polymers produced were of low DP. As it was thought that the low DP was affecting the alignment properties of the SCLC polymers, a variety of alternative synthetic strategies were attempted to overcome this problem.

2.1 Introduction to Experimental

The structure of all the compounds were confirmed by a combination of NMR spectroscopy (JEOL JNM-GX-270 MHz spectrometer), IR spectroscopy (Perkin-Elmer 783 grating spectrophotometer) mass spectrometry (Finnigan-MAT 1020G/MS spectrometer) and optical rotation (Optical Activity AA-10 automatic polarimeter). The purity of the compounds was checked by TLC (single spot) or by HPLC (25 × 0.46 cm, 5 μm, C 18 Microsorb column, acetonitrile, >99%) and for the SCLC polymers by gpc [5 μm, 30 × 0.75 cm, 2 × mixed D-PL columns, calibrated using polystyrene standards (Mp = 1000 - 430500), toluene; no monomer present]. The transitions for liquid crystalline phases were determined by DSC (Perkin-Elmer DSC 7 with data station and cooling accessory) and the LC phases were identified by optical microscopy (Olympus BH2 polarising microscope in conjunction with a Mettler FP52 hot-stage and FP5 control unit).

All NMR experiments were carried out with the sample in $CDCl_3$ solution. All IR experiments were carried out with the sample between KBr plates, liquids as a thin film and solids in a KBr disc. All specific optical rotation measurements were obtained with the sample in solution in $CHCl_3$, between 23 °C and 25 °C.

Apart from those preparations which are specifically referenced, all other preparations were carried out following personal communication with my colleagues, using standard procedures as developed within the research group at Hull.

2.2 Abbreviations

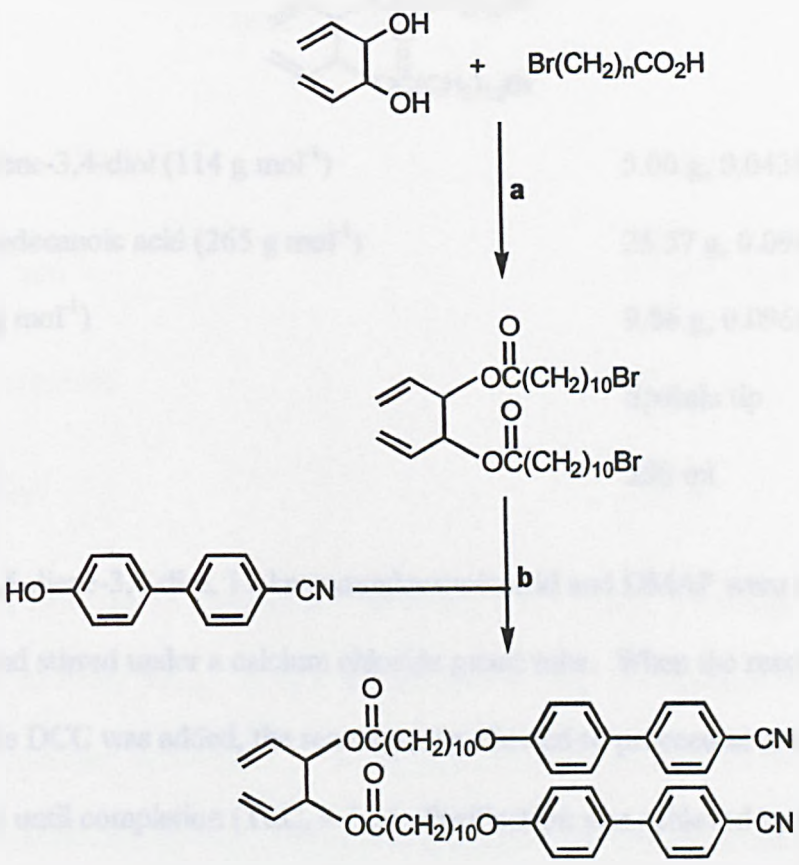
CHB	4-cyano-4'-hydroxybiphenyl
DCC	*N*,*N*'-dicyclohexylcarbodiimide
DCM	dichloromethane
DEAD	diethyl azodicarboxylate
DMAP	*N*,*N*-dimethyl-4-amino pyridine
DME	dimethoxyethane
THF	tetrahydrofuran
TLC	thin layer chromatography

2.3 Preparation of Anhydrous Solvents

Anhydrous butanone was prepared by storing the solvent over type 4A molecular sieves. When anhydrous DCM was required, it was simply taken from a freshly opened bottle. Anhydrous THF was prepared by distillation under an atmosphere of dry nitrogen from sodium and benzophenone.

2.4 Synthetic Schemes and Experimental

2.4.1 Series 1



Scheme 1

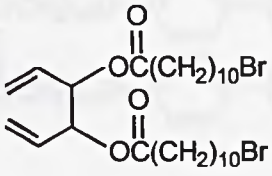
a DCC, DMAP, DCM (dry).

b Potassium carbonate (dry), butanone (dry).

Compounds Synthesised From Scheme 1

Compound **1.1**

Hexa-1,5-dien-3,4-yl bis-11-bromoundecenoate



Hexa-1,5-diene-3,4-diol (114 g mol^{-1})	5.00 g, 0.0438 mol
11-Bromoundecanoic acid (265 g mol^{-1})	25.57 g, 0.0964 mol
DCC (206 g mol^{-1})	9.86 g, 0.0964 mol
DMAP	Spatula tip
DCM (dry)	250 ml

The hexa-1,5-diene-3,4-diol, 11-bromoundecanoic acid and DMAP were added to the dry DCM and stirred under a calcium chloride guard tube. When the reactants had dissolved the DCC was added, the reaction was allowed to proceed at room temperature until completion (TLC, ≈ 1 h). Purification was achieved by pouring the reaction mixture onto a wide (≈ 10 cm) column of dry silica gel and eluting the column with DCM. The solvent was removed *in vacuo* to yield a white waxy solid.

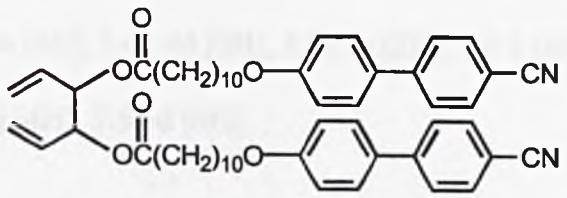
Yield = 22.34 g, 84 %.

IR $\nu_{max}(cm^{-1})$: 930, 980, 1240, 1640, 1730, 2850, 2920.

^1H NMR: δ 1.3 m [24H], 1.6 m [4H], 1.9 m [4H], 2.3 t [4H], 3.4 t [4H], 5.30 m [4H], 5.41 dd [2H], 5.80 m [2H].

Compound **1.2**

Hexa-1,5-dien-3,4-yl bis-11-(4-cyanobiphenyl-4'-yloxy)undecanoate



Compound **1.1** (608 g mol^{-1})	22.00 g, 0.0362 mol
CHB (195 g mol^{-1})	15.60 g, 0.080 mol
Potassium carbonate	36 g
Butanone (dry)	250 ml

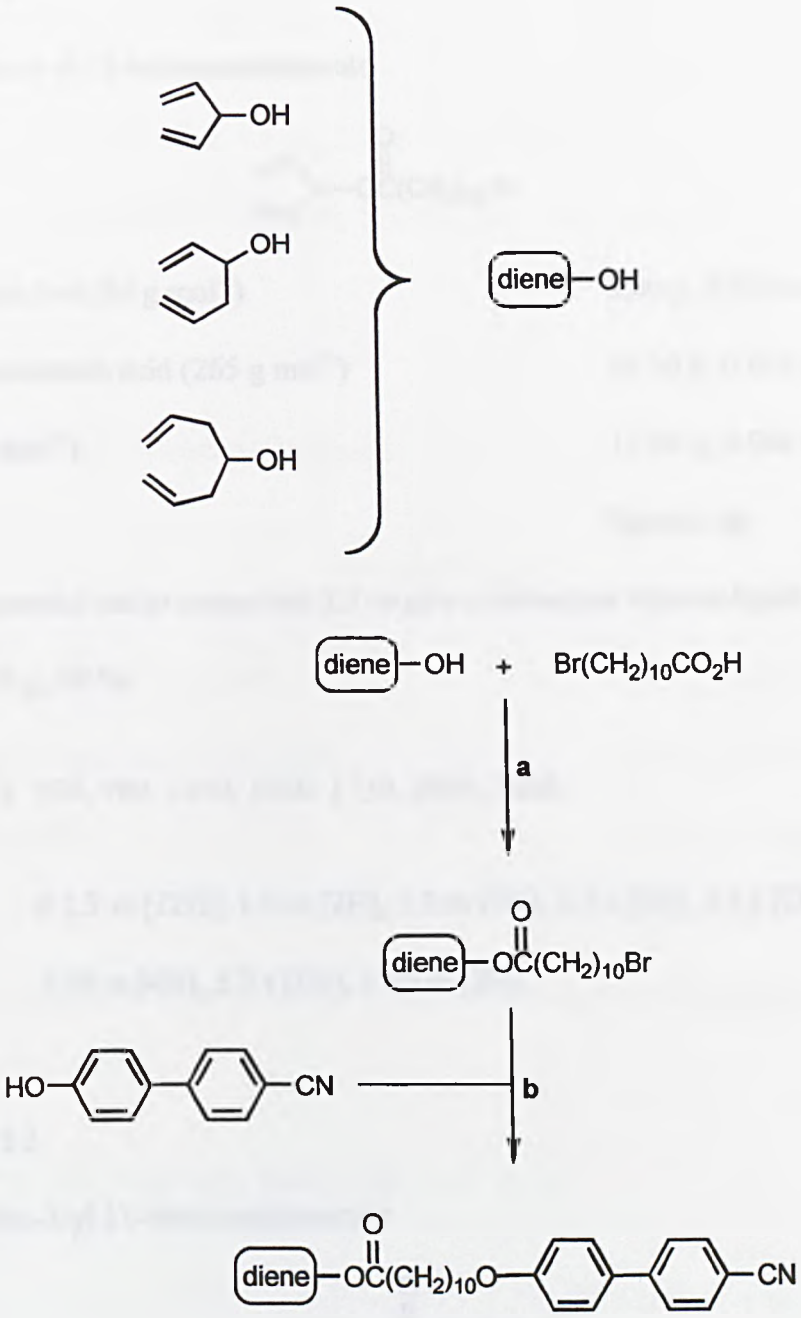
The reagents listed above were stirred vigorously under reflux. Protection from atmospheric moisture was given by a calcium guard tube. The reaction was allowed to proceed until completion (TLC, ≈ 24 h). The inorganic solids were filtered off and washed with acetone (100 ml). The organic extracts were combined and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using silica gel eluted with DCM. The solvent was removed *in vacuo* to give a white solid, which was dissolved in the minimum amount of DCM. The solution was added dropwise to rapidly stirred petrol (b.p. 40-60 °C, 250 ml) from which the product precipitated. The precipitate was filtered off and washed with petrol (b.p. 40-60 °C, 25 ml), and dried *in vacuo* to yield a white powder.

Yield = 19.97 g, 66 %.

IR $\nu_{max}(cm^{-1})$: 530, 820, 930, 1000, 1180, 1250, 1490, 1600, 1640, 1730, 2210, 2850, 2920.

^1H NMR: δ 1.3 m [24H], 1.6 m [4H], 1.9 m [4H], 2.3 t [4H], 4.0 t [4H], 5.30 m [4H], 5.41 dd [2H], 5.80 m [2H], 7.0 d [4H], 7.5 d [4H], 7.63 d [4H], 7.69 d [4H].

2.4.2 Series 2



Scheme 2

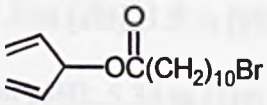
a DCC, DMAP, DCM (dry).

b Potassium carbonate (dry), butanone (dry).

Compounds Synthesised From Scheme 2

Compound **2.1**

Penta-1,4-dien-3-yl 11-bromoundecanoate



Penta-1,4-dien-3-ol (84 g mol^{-1})	5.00 g, 0.060 mol
11-Bromoundecanoic acid (265 g mol^{-1})	18.30 g, 0.069 mol
DCC (206 g mol^{-1})	13.60 g, 0.066 mol
DMAP	Spatula tip

Preparation carried out as compound **1.1** to give a colourless viscous liquid.

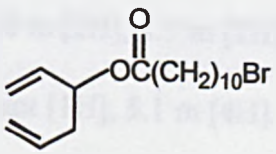
Yield = 19.55 g, 99 %.

IR ν_{max}(cm^{-1}): 930, 980, 1240, 1640, 1730, 2850, 2920.

^{1}H NMR δ 1.3 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 3.4 t [2H], 5.30 m [4H], 5.7 t [1H], 5.80 m [2H].

Compound **2.2**

Hexa-1,5-dien-3-yl 11-bromoundecanoate



Hexa-1,5-dien-3-ol (98 g mol^{-1})	5.00 g, 0.051 mol
11-Bromoundecanoic acid (265 g mol^{-1})	15.60 g, 0.059 mol
DCC (206 g mol^{-1})	11.60 g, 0.056 mol

Preparation carried out as compound **1.1** to give a colourless viscous liquid.

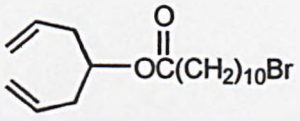
Yield = 17.94 g, 100 %.

IR $\nu_{max}(cm^{-1})$: 930, 980, 1240, 1640, 1730, 2850, 2920.

^1H NMR δ 1.3 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 dd [2H], 3.4 t [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H].

Compound **2.3**

Hepta-1,6-dien-4-yl 11-bromoundecanoate



Hepta-1,6-dien-4-ol (112 g mol^{-1})	5.00 g, 0.045 mol
11-Bromoundecanoic acid (265 g mol^{-1})	13.80 g, 0.052 mol
DCC (206 g mol^{-1})	10.30 g, 0.50 mol
DMAP	Spatula tip

Preparation carried out as compound **1.1** to give a colourless viscous liquid.

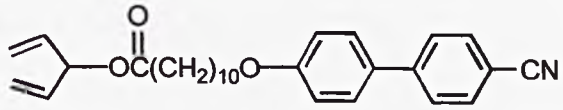
Yield = 14.92 g, 93 %.

IR $\nu_{max}(cm^{-1})$: 930, 980, 1240, 1640, 1730, 2850, 2920.

^1H NMR δ 1.3 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 m [4H], 3.4 t [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H].

Compound **2.4**

Penta-1,4-dien-3-yl 11-(4-cyanobiphenyl-4'-yloxy)undecanoate



Compound **2.1** (331 g mol^{-1})	10.00 g, 0.030 mo
CHB (195 g mol^{-1})	6.44 g, 0.033 mol
Potassium carbonate	15 g
Butanone (dry)	125 ml

Preparation carried out as for compound **1.2** to give a white powder.

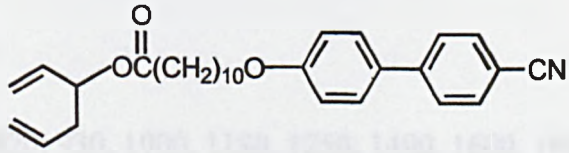
Yield = 8.68 g, 65 %.

IR ν_{max}(cm^{-1}): 530, 820, 930, 1000, 1180, 1250, 1490, 1600, 1640, 1730, 2210, 2850, 2920.

^{1}H NMR δ 1.3 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 4.0 t [2H], 5.30 m [4H], 5.7 t [1H], 5.80 m [2H], 7.0 d [2H], 7.5 d [2H], 7.63 d [2H], 7.69 d [2H].

Compound **2.5**

Hexa-1,5-dien-3-yl 11-(4-cyanobiphenyl-4'-yloxy)undecanoate



Compound **2.2** (345 g mol^{-1})	10.35 g, 0.030 mol
CHB (195 g mol^{-1})	8.80 g, 0.033 mol
Potassium carbonate	15 g

Butanone (dry) 125 ml

Preparation carried out as for compound **1.2** to give a white powder.

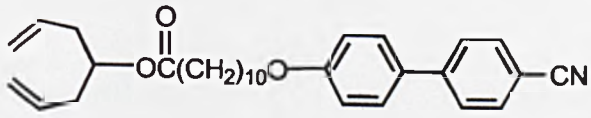
Yield = 9.29 g, 67 %.

IR $\nu_{max}(cm^{-1})$: 530, 820, 930, 1000, 1180, 1250, 1490, 1600, 1640, 1730, 2210, 2850, 2920.

^1H NMR δ 1.3 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 dd [2H], 4.0 t [2H], 5.13 m [4H], 5.3 m [1H], 5.7 t [2H], 7.0 d [2H], 7.5 d [2H], 7.63 d [2H], 7.69 d [2H].

Compound **2.6**

Hepta-1,6-dien-4-yl 11-(4-cyanobiphenyl-4'-yloxy)undecanoate



Compound **2.3** (359 g mol^{-1}) 5.39 g, 0.015 mol

CHB (195 g mol^{-1}) 3.32 g, 0.017 mol

Potassium carbonate 8 g

Butanone (dry) 125 ml

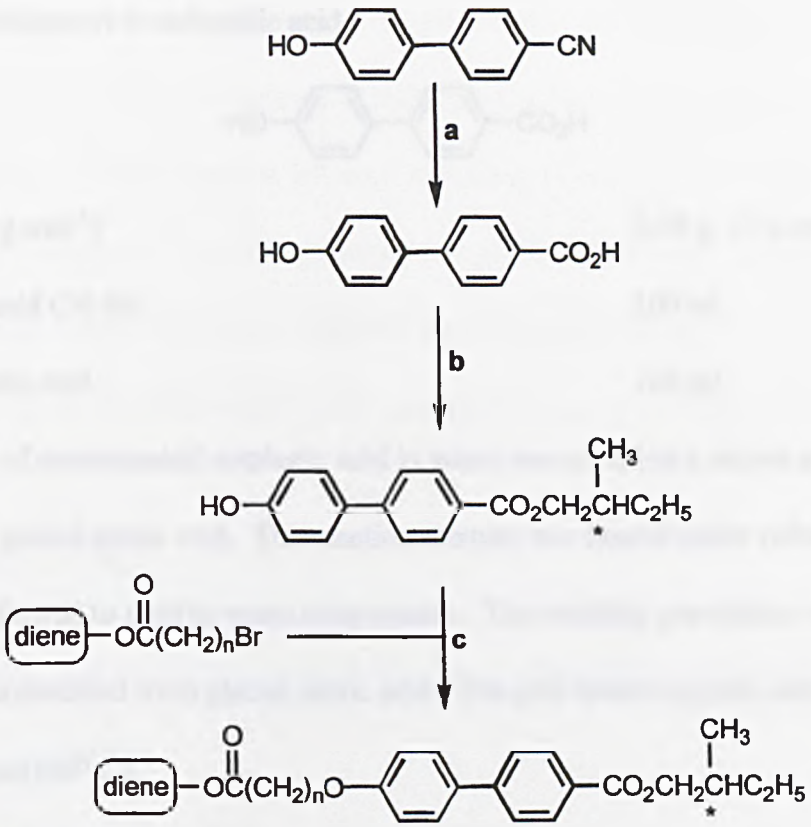
Preparation carried out as for compound **1.2** to give a white powder.

Yield = 4.4 g, 62 %.

IR $\nu_{max}(cm^{-1})$: 530, 820, 930, 1000, 1180, 1250, 1490, 1600, 1640, 1730, 2210, 2850, 2920.

^{1}H NMR δ 1.3 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 m [4H], 4.0 t [2H], 5.0 quint [1H] 5.1 m [4H], 5.6 m [2H], 7.0 d [2H], 7.5 d [2H], 7.63 d [2H], 7.69 d [2H].

2.4.3 Series 3



Scheme 3

a Concentrated sulphuric acid, glacial acetic acid, water.

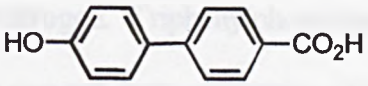
b (*S*)-(-)-2-Methylbutan-1-ol, DEAD, triphenylphosphine, THF (dry).

c Potassium carbonate (dry), butanone (dry).

Compounds Synthesised From Scheme 3

Compound **3.1**

4'-Hydroxybiphenyl-4-carboxylic acid



CHB (195 g mol^{-1})	5.00 g, 25.6 mmol
Sulphuric acid (50 %)	100 ml
Glacial acetic acid	100 ml

A solution of concentrated sulphuric acid in water was added to a stirred suspension of CHB in glacial acetic acid. The reaction mixture was heated under reflux for 48 h, then was allowed to cool to room temperature. The resulting precipitate was filtered off and recrystallised from glacial acetic acid. The pale brown crystals were filtered off and dried (80° C).

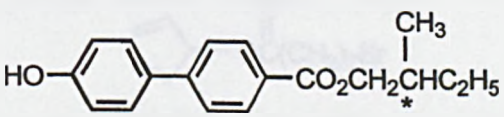
Yield = 3.88 g, 71 %.

IR ν_{max}(cm^{-1}): 660, 770, 830, 1190, 1230, 1300, 1420, 1600, 1670, 3400.

^{1}H NMR: δ 6.9 d [2H], 7.6 d [2H], 7.7 d [2H], 8.0 d [2H].

Compound **3.2**

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



Compound **3.1** (214 g mol^{-1})	5.00 g, 23.4 mmol
(*S*)-(-)-2-Methylbutan-1-ol (88 g mol^{-1})	2.06 g, 23.4 mmol

Triphenylphosphine (262 g mol^{-1})	6.12 g, 23.4 mmol
DEAD (174 g mol^{-1})	4.07 g, 23.4 mmol
THF (dry)	100 ml

Compound **3.1**, (*S*)-(-)-2-methylbutan-1-ol and DEAD were dissolved in THF, and stirred vigorously under dry nitrogen. Triphenylphosphine was added to the solution in one portion. The reaction was left until completion (TLC, 1 h) then the solvent was removed *in vacuo*. The crude product was purified by column chromatography using silica gel and eluting firstly with DCM and secondly with ethyl acetate/petrol (b.p. 40-60 °C) (1:1). The solvent was removed *in vacuo* to yield an off white waxy solid.

Yield = 6.11 g, 92 %.

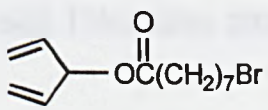
IR $\nu_{max}(cm^{-1})$: 770, 830, 1120, 1190, 1280, 1440, 1490, 1520, 1600, 1680, 2960, 3400.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.2 m [1H], 1.6 m [1H], 1.9 m [1H], 4.2 m [2H], 6.9 d [2H], 7.5 d [2H], 7.6 d [2H], 8.1 d [2H].

OR: $[\alpha]_D = +5.08°$.

Compound **3.3**

Penta-1,4-dien-3-yl 8-bromooctanoate



Penta-1,4-dien-3-ol (84 g mol^{-1})	1.90 g, 22.4 mmol
8-Bromooctanoic acid (223 g mol^{-1})	5.00 g, 22.4 mmol

DCC (206 g mol^{-1}) 5.10 g, 24.6 mmol

DMAP Spatula tip

Preparation carried out as for compound **1.1** to yield a colourless viscous liquid.

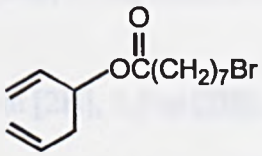
Yield = 5.28 g, 82 %.

IR $\nu_{max}(cm^{-1})$: 930, 980, 1240, 1640, 1730, 2850, 2920.

^1H NMR: δ1.3 m [6H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 3.4 t [2H], 5.30 m [4H], 5.7 t [1H], 5.80 m [2H].

Compound **3.4**

Hexa-1,5-dien-3-yl 8-bromooctanoate



Hexa-1,5-dien-3-ol (98 g mol^{-1}) 2.20 g, 22.4 mmol

8-Bromooctanoic acid (223 g mol^{-1}) 5.00 g, 22.4 mmol

DCC (206 g mol^{-1}) 5.10 g, 24.6 mmol

DMAP Spatula tip

Preparation carried out as for compound **1.1** to yield a colourless viscous liquid.

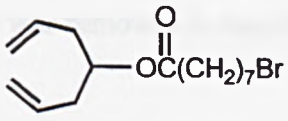
Yield = 6.08 g, 90 %.

IR $\nu_{max}(cm^{-1})$: 930, 980, 1240, 1640, 1730, 2850, 2920.

^1H NMR: δ1.3 m [6H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 dd [2H], 3.4 t [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H].

Compound **3.5**

Hepta-1,6-dien-4-yl 8-bromooctanoate



Hepta-1,6-dien-4-ol (112 g mol^{-1})	2.51 g, 22.4 mmol
8-Bromooctanoic acid (223 g mol^{-1})	5.00 g, 22.4 mmol
DCC (206 g mol^{-1})	5.10 g, 24.6 mmol
DMAP	Spatula tip

Preparation carried out as for compound **1.1** to yield a colourless viscous liquid.

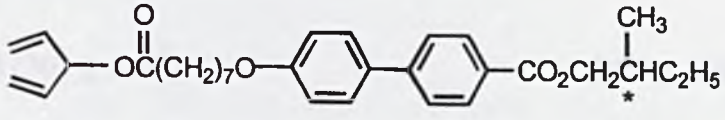
Yield = 5.56 g, 78 %.

IR ν_{max}(cm^{-1}): 930, 980, 1240, 1640, 1730, 2850, 2920.

^{1}H NMR: δ1.3 m [6H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 m [4H], 3.4 t [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H].

Compound **3.6**

(*S*)-2-Methylbutyl 4'-(penta-1,4-dien-3-yloxycarbonylheptyloxy)biphenyl-4-carboxylate



Compound **3.3** (289 g mol^{-1})	2.00 g, 6.90 mmol
Compound **3.2** (284 g mol^{-1})	1.97 g, 6.90 mmol
Potassium carbonate	5 g
Butanone	100 ml

Preparation carried out as compound **1.2** with the exception of the purification steps. The crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed in vacuo to yield a colourles, viscous liquid.

Yield = 2.90 g, 85 %.

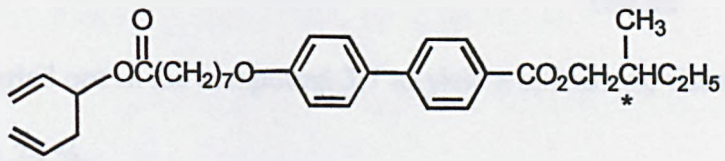
IR $\nu_{max}(cm^{-1})$: 770, 830, 1100, 1190, 1270, 1460, 1490, 1520, 1600, 1710, 1730, 2860, 2920.

^1H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.4 m [10H], 1.9 m [3H], 2.3 t [2H], 4.0 t [2H], 4.2 m [2H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 7.5 d [2H], 7.6 d [2H], 8.1 d [2H].

OR: $[\alpha]_D = +3.43°$.

Compound **3.7**

(*S*)-2-Methylbutyl 4'-(hexa-1,5-dien-3-yloxycarbonylheptyloxy)biphenyl-4-carboxylate



Compound **3.4** (303 g mol^{-1})	2.00 g, 6.60 mmol
Compound **3.2** (284 g mol^{-1})	1.87 g, 6.60 mmol
Potassium carbonate	5 g
Butanone	100 ml

Preparation carried out as for compound **3.7** to yield a colourless, viscous liquid.

Yield = 2.94 g, 88 %.

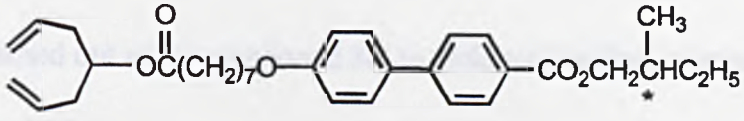
IR $\nu_{max}(cm^{-1})$: 770, 830, 1100, 1190, 1270, 1460, 1490, 1520, 1600, 1710, 1730, 2860, 2920.

^1H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.4 m [10H], 1.9 m[3H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 4.2 m [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 6.9 d [2H], 7.5 d [2H], 7.6 d [2H], 8.1 d [2H].

OR: $[\alpha]_D = +1.83°$.

Compound **3.8**

(*S*)-2-Methylbutyl 4'-(hepta-1,6-dien-4-yloxycarbonylheptyloxy)biphenyl-4-carboxylate



Compound **3.5** (317 g mol^{-1})	2.00 g, 6.31 mmol
Compound **3.2** (284 g mol^{-1})	1.79 g, 6.31 mmol
Potassium carbonate	5 g
Butanone	100 ml

Preparation carried out as for compound **3.7** to yield a colourless, viscous liquid.

Yield = 2.43 g, 74 %.

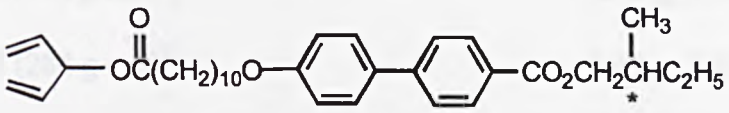
IR $\nu_{max}(cm^{-1})$: 770, 830, 1100, 1190, 1270, 1460, 1490, 1520, 1600, 1710, 1730, 2860, 2920.

^1H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.4 m [10H], 1.9 m [3H], 2.3 t [2H], 2.4 t [4H], 4.0 t [2H], 4.2 m [2H], 5.0 m [1H], 5.1 quint [4H], 5.75 m [2H], 6.9 d [2H], 7.5 d [2H], 7.6 d [2H], 8.1 d [2H].

OR: $[\alpha]_D = +1.07°$.

Compound **3.9**

(*S*)-2-Methylbutyl 4'-(penta-1,4-dien-3-yloxycarbonyldecyloxy)biphenyl-4-carboxylate



Compound **2.1** (331 g mol^{-1})	1.09 g, 3.28 mmol
Compound **3.2** (284 g mol^{-1})	0.93 g, 3.28 mmol
Potassium carbonate	5 g
Butanone	100 ml

Preparation carried out as for compound **3.7** to yield a colourless, viscous liquid.

Yield = 1.32 g, 75 %.

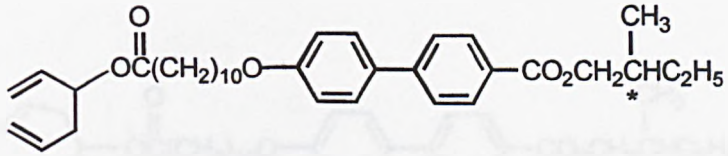
IR $\nu_{max}(cm^{-1})$: 770, 830, 1100, 1190, 1270, 1460, 1490, 1520, 1600, 1710, 1730, 2860, 2920.

^1H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.4 m [16H], 1.9 m [3H], 2.3 t [2H], 4.0 t [2H], 4.2 m [2H], 5.3 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 7.5 d [2H], 7.6 d [2H], 8.1 d [2H].

OR: $[\alpha]_D = +2.59°$.

Compound **3.10**

(*S*)-2-Methylbutyl 4'-(hexa-1,5-dien-3-yloxycarbonyldecyloxy)biphenyl-4-carboxylate



Compound **2.2** (345 g mol^{-1})	1.15 g, 3.33 mmol
Compound **3.2** (284 g mol^{-1})	0.95 g, 3.33 mmol
Potassium carbonate	5 g
Butanone	100 ml

Preparation carried out as for compound **3.7** to yield a colourless, viscous liquid.

Yield = 1.44 g, 77 %.

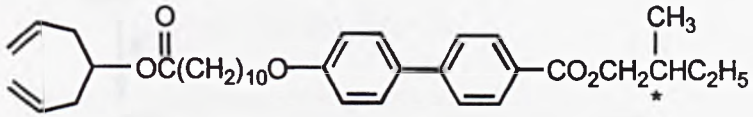
IR ν_{max}(cm^{-1}): 770, 830, 1100, 1190, 1270, 1460, 1490, 1520, 1600, 1710, 1730, 2860, 2920.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.4 m [16H], 1.9 m [3H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 4.2 m [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 6.9 d [2H], 7.5 d [2H], 7.6 d [2H], 8.1 d [2H].

OR: $[\alpha]_D$ = + 2.05°.

Compound **3.11**

(*S*)-2-Methylbutyl 4'-(hepta-1,6-dien-4-yl oxycarbonyldecyloxy)biphenyl-4-carboxylate



Compound **2.3** (359 g mol^{-1})	1.13 g, 3.15 mmol
Compound **3.2** (284 g mol^{-1})	0.89 g, 3.15 mmol
Potassium carbonate	5 g
Butanone	100 ml

Preparation carried out as for compound **3.7** to yield a colourless, viscous liquid.

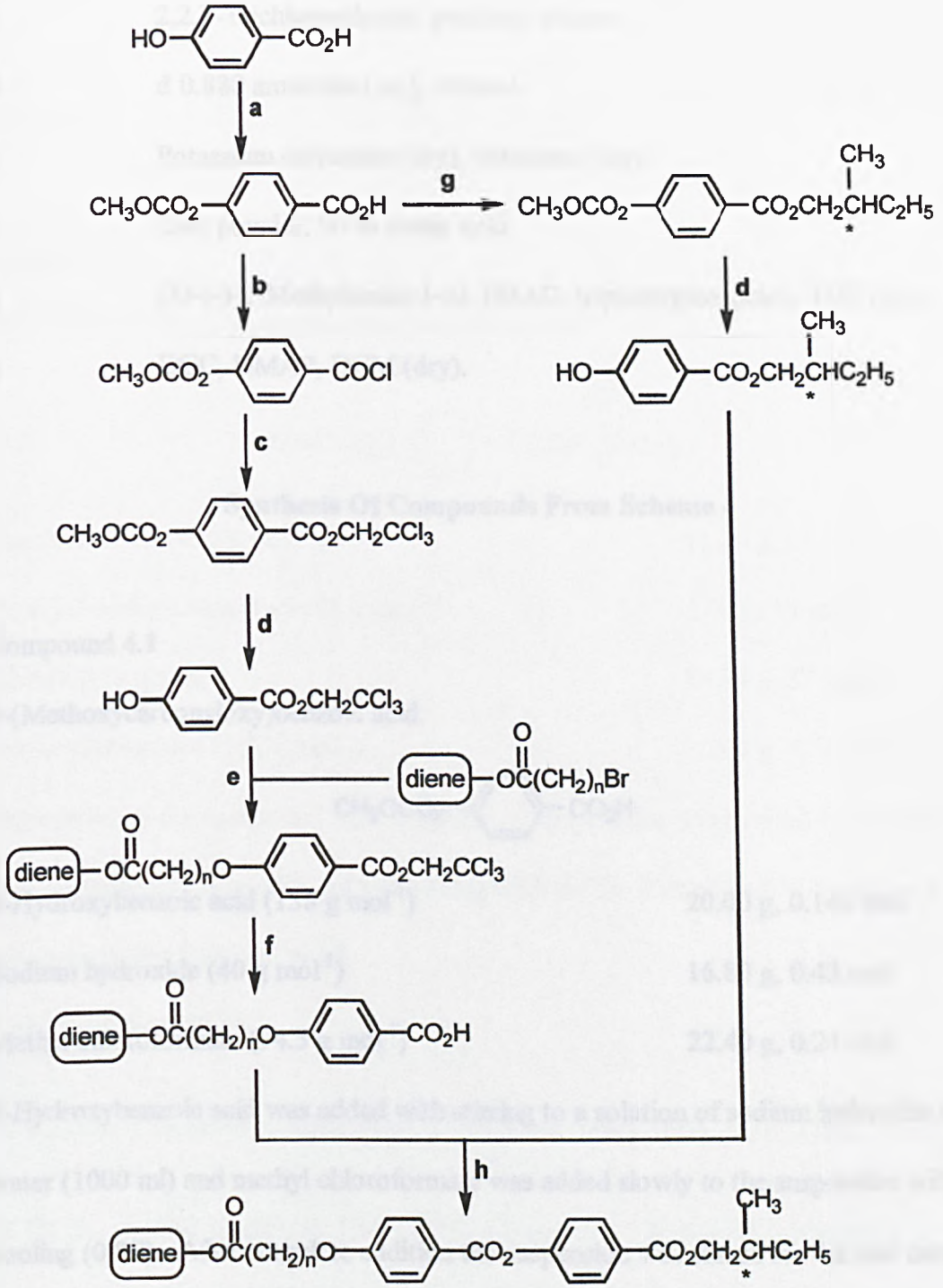
Yield = 1.20 g, 67 %.

IR ν_{max}(cm^{-1}): 770, 830, 1100, 1190, 1270, 1460, 1490, 1520, 1600, 1710, 1730, 2860, 2920.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.4 m [16H], 1.9 m [3H], 2.3 t [2H], 2.4 t [4H], 4.0 t [2H], 4.2 m [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 6.9 d [2H], 7.5 d [2H], 7.6 d [2H], 8.1 d [2H].

OR: $[\alpha]_D$ = + 1.74°.

2.4.4 Series 4



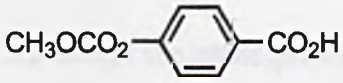
Scheme 4

a	Methyl chloroformate, sodium hydroxide, water.
b	Thionyl chloride.
c	2,2,2-Trichloroethanol, pyridine, toluene.
d	d 0.880 ammonia (aq.), ethanol.
e	Potassium carbonate (dry), butanone (dry).
f	Zinc powder, 90 % acetic acid.
g	(*S*)-(-)-2-Methylbutan-1-ol, DEAD, triphenylphosphine, THF (dry).
h	DCC, DMAP, DCM (dry).

Synthesis Of Compounds From Scheme 4

Compound **4.1**

4-(Methoxycarbonyloxy)benzoic acid



4-Hydroxybenzoic acid (138 g mol^{-1})	20.00 g, 0.146 mol
Sodium hydroxide (40 g mol^{-1})	16.80 g, 0.42 mol
Methyl chloroformate (94.5 g mol^{-1})	22.40 g, 0.24 mol

4-Hydroxybenzoic acid was added with stirring to a solution of sodium hydroxide in water (1000 ml) and methyl chloroformate was added slowly to the suspension with cooling (0 °C). After complete addition the suspension was stirred for 4 h and then allowed to warm to room temperature. The pH was adjusted to 4 by the addition of hydrochloric acid (50 %). The white precipitate was filtered off, recrystallised from ethanol and dried (80 °C) to yield a white crystalline solid.

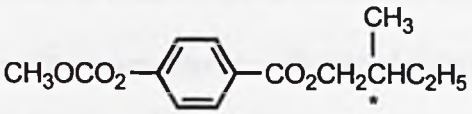
Yield = 27.10 g, 95 %.

IR $\nu_{max}(cm^{-1})$: 660, 770, 850, 940, 1220, 1260, 1440, 1600, 1680, 1750, 1770, 2960.

^1H NMR: δ 3.95 s [3H], 7.3 d [2H], 8.2 d [2H].

Compound **4.2**

(*S*)-2-Methylbutyl 4-(methoxycarbonyloxy)benzoate



Compound **4.1** (196 g mol^{-1})	11.20 g, 57 mmol
(*S*)-(-)-2-Methylbutan-1-ol (88 g mol^{-1})	5.00 g, 57 mmol
DEAD (174 g mol^{-1})	14.94 g, 57 mmol
Triphenylphophine (262 g mol^{-1})	10.00 g, 57 mmol

Preparation as for compound **3.2** except the crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* to yield a pale yellow oil.

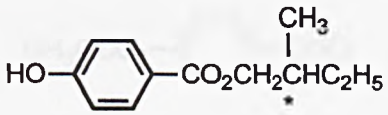
Yield = 14.06 g, 93 %.

IR $\nu_{max}(cm^{-1})$: 570, 940, 1020, 1110, 1210, 1260, 1440, 1600, 1710, 1760, 2960.

^1H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.2 m [1H], 1.6 m [1H], 1.9 m [1H], 3.95 s [3H], 4.2 m [2H], 7.3 d [2H], 8.8 d [2H].

Compound **4.3**

(S)-2-Methylbutyl 4-hydroxybenzoate



Compound **4.2** (266 g mol^{-1})	14.06 g, 52.8 mmol
Ethanol	100 ml
d 0.880 Ammonia solution	50 ml

Compound **4.2** was dissolved in ethanol and to the stirred solution was added ammonia solution. The mixture was stirred until completion (TLC, 1 h) and the solvent was removed *in vacuo*. The crude product was taken up into di-ethyl ether (100 ml) and washed with saturated sodium hydrogen carbonate solution (100 ml), followed by water (2 × 50 ml). The organic layer was dried over magnesium sulphate and the solvent was removed *in vacuo* to give a viscous pale yellow oil.

Yield = 10.7 g, 97 %.

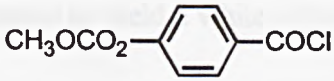
IR $\nu_{max}(cm^{-1})$: 640, 770, 850, 1120, 1160, 1230, 1440, 1510, 1600, 1680, 2960, 3360.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.2 m [1H], 1.6 m [1H], 1.9 m [1H], 4.2 m [2H], 6.9 d [2H], 8.0 d [2H].

OR: $[\alpha]_D$ = - 6.80°.

Compound **4.4**

4-(Methoxycarbonyloxy)benzoyl chloride



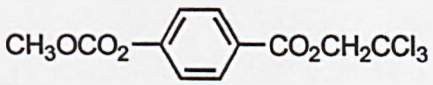
Compound **4.1** (196 g mol^{-1})	20.00 g, 0.10 mol
Thionyl chloride	100 ml

Compound **4.1** was suspended in thionyl chloride with stirring under dry nitrogen. The reaction mixture was heated under reflux for 3 h, by which time a clear solution had formed. The solvent was removed *in vacuo* to give an off white solid. The crude product was used without further purification.

Yield = 21.50 g, 100 %.

Compound **4.5**

2,2,2-Trichloroethyl 4-(methoxycarbonyloxy)benzoate



Compound **4.4** (214.5 g mol^{-1})	21.50 g, 0.10 mol
2,2,2-Trichloroethanol (149.4 g mol^{-1})	14.90 g, 0.010 mol
Pyridine (dry) (79 g mol^{-1})	7.90 g, 0.01 mol
Toluene (dry)	150 ml

Compound **4.4** was added to toluene and the suspension was stirred under dry nitrogen. 2,2,2-Trichloroethanol and pyridine were added and the mixture was heated under reflux for 2 h, by which time a clear solution had been produced. The mixture was cooled to room temperature and was added to water (200 ml) and was extracted with diethyl ether (2 × 200 ml). The combined organic extracts were wased

with hydrochloric acid (10 %, 100 ml) and then dried (magnesium sulphate). The solvent was removed *in vacuo* and the crude product was recrystallised from petrol (b.p. 40-60 °C) and dried *in vacuo* to yield a white crystalline solid.

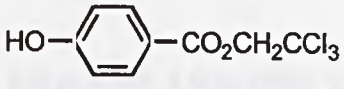
Yield = 23.50 g, 72 %.

IR $\nu_{max}(cm^{-1})$: 570, 720, 940, 1010, 1120, 1160, 1210, 1260, 1440, 1600, 1720, 1760, 2960.

^1H NMR: δ 3.95 s [3H], 5.0 m [2H], 7.9 d [2H], 8.2 d [2H].

Compound **4.6**

2,2,2-Trichloroethyl 4-hydroxybenzoate



Compound **4.5** (327.4 g mol^{-1})	23.50 g, 0.072 mol
Ethanol	500 ml
d 0.880 Ammonia solution	100 ml

Preparation carried out as for compond **4.3** to give a white, waxy solid.

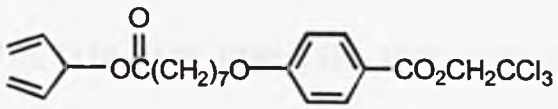
Yield = 19.40 g, 100 %.

IR $\nu_{max}(cm^{-1})$: 720, 770, 1120, 1160, 1230, 1280, 1440, 1510, 1590, 1600, 1720, 3320.

^1H NMR: δ 4.9 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.7**

2,2,2-Trichloroethyl 4-(penta-1,4-dien-3-yloxycarbonylheptyloxy)benzoate



Compound **3.3** (289 g mol^{-1})	2.50 g, 8.70 mmol
Compound **4.6** (269.4) g mol^{-1}	2.33 g, 8.70 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a yellow oil.

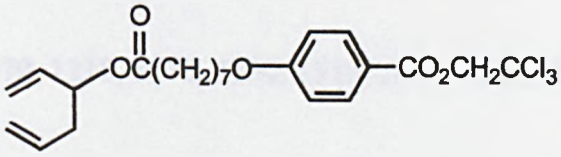
Yield = 3.95 g, 95 %.

IR ν_{max}(cm^{-1}): 720, 770, 1110, 1170, 1250, 1510, 1600, 1730, 2840, 2920.

^{1}H NMR: δ 1.4 m [6H], 1.6 m [2H], 1.9 m [2H], 2.4 t [2H], 4.0 t [2H], 5.0 s [2H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.8**

2,2,2-Trichloroethyl 4-(hexa-1,5-dien-3-yloxycarbonylheptyloxy)benzoate



Compound **3.4** (303 g mol^{-1})	2.50 g, 8.30 mmol
Compound **4.6** (269.4 g mol^{-1})	2.23 g, 8.30 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a yellow oil.

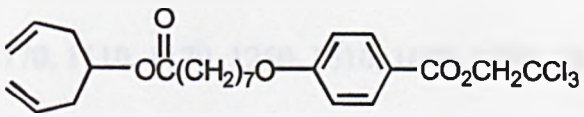
Yield = 3.58 g, 88 %.

IR $\nu_{max}(cm^{-1})$: 720, 770, 1110, 1170, 1250, 1510, 1600, 1730, 2840, 2920.

^1H NMR: δ 1.4 m [6H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 5.0 s [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.9**

2,2,2-Trichloroethyl 4-(hepta-1,6-dien-4-yloxycarbonylheptyloxy)benzoate



Compound **3.5** (317 g mol^{-1})	2.50 g, 7.89 mmol
Compound **4.6** (269.4 g mol^{-1})	2.13 g, 7.89 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a yellow oil.

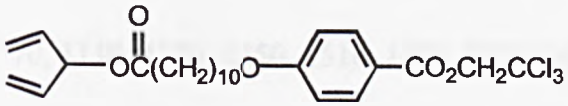
Yield = 3.90 g, 98 %.

IR $\nu_{max}(cm^{-1})$: 720, 770, 1110, 1170, 1250, 1510, 1600, 1730, 2840, 2920.

^1H NMR: δ 1.4 m [6H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 m [4H], 4.0 t [2H], 4.95 s [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.10**

2,2,2-Trichloroethyl 4-(penta-1,4-dien-3-yloxycarbonyldecyloxy)benzoate



Compound **2.1** (331 g mol^{-1})	2.00 g, 6.04 mmol
Compound **4.6** (269.4 g mol^{-1})	1.63 g, 6.04 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a yellow oil.

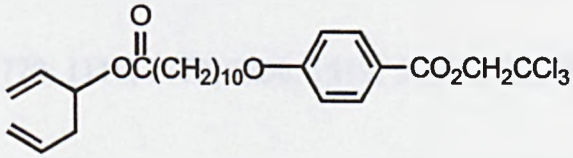
Yield = 2.63 g, 84 %.

IR ν_{max}(cm^{-1}): 720, 770, 1110, 1170, 1250, 1510, 1600, 1730, 2840, 2920.

^{1}H NMR: δ 1.4 m [12H], 1.6 m [2H], 1.9 m [2H], 2.4 t [2H], 4.0 t [2H], 5.0 s [2H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.11**

2,2,2-Trichloroethyl 4-(hexa-1,5-dien-3-yloxycarbonyldecyloxy)benzoate



Compound **2.2** (345 g mol^{-1})	2.00 g, 5.80 mmol
Compound **4.6** (269.4 g mol^{-1})	1.72 g, 6.38 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a yellow oil.

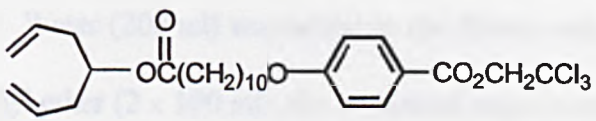
Yield = 2.12 g, 68 %.

IR $\nu_{max}(cm^{-1})$: 720, 770, 1110, 1170, 1250, 1510, 1600, 1730, 2840, 2920.

^{1}H NMR: δ 1.4 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 5.0 s [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.12**

2,2,2-Trichloroethyl 4-(hepta-1,6-dien-4-yloxycarbonyldecyloxy)benzoate



Compound **2.3** (359 g mol^{-1})	2.00 g, 5.57 mmol
Compound **4.6** (269.4 g mol^{-1})	1.50 g, 5.57 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a yellow oil.

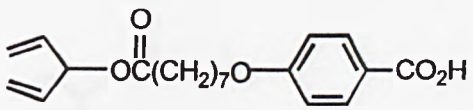
Yield = 2.67 g, 88 %.

IR $\nu_{max}(cm^{-1})$: 720, 770, 1110, 1170, 1250, 1510, 1600, 1730, 2840, 2920.

^{1}H NMR: δ 1.4 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 m [4H], 4.0 t [2H], 4.95 s [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.13**

4-(penta-1,4-dien-3-yloxycarbonylheptyloxy)benzoic acid



Compound **4.7** (477.4 g mol^{-1})	3.95 g, 8.27 mmol
Zinc powder (65.4 g mol^{-1})	5.41 g, 82.7 mmol
Acetic acid (90 %)	30 ml

Compound **4.7** was dissolved in acetic acid (90 %) at room teperature and the zinc was added in one portion with vigorous stirring. Upon completion (TLC, 0.5 h) the zinc was filtered off and washed with glacial acetic acid (30 ml), water (30 ml) and di-ethyl ether (100 ml). Water (200 ml) was added to the filtrate which was then extracted with di-ethyl ether (2 × 100 ml), the combined organic extracts were dried over magnesium sulphate. The solvent was removed *in vacuo* and the crude product was purified by column chromatography using a short (50 mm) column of silica and eluting first with DCM then with ethyl acetate. The solvent was removed *in vacuo* to give an off white solid.

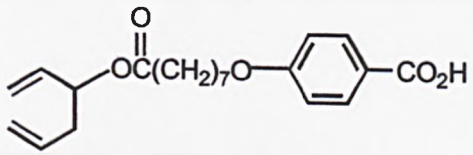
Yield = 2.13 g, 78 %.

IR ν_{max}(cm^{-1}): 770, 930, 1170, 1250, 1430, 1510, 1600, 1670, 1730, 2840, 2920, 3400.

^{1}H NMR: δ 1.4 m [6H], 1.6 m [2H], 1.9 m [2H], 2.4 t [2H], 4.0 t [2H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.14**

4-(hexa-1,5-dien-3-yloxycarbonylheptyloxy)benzoic acid



Compound **4.8** (491.4 g mol^{-1})	3.50 g, 7.12 mmol
Zinc powder (65.4 g mol^{-1})	4.66 g, 71.2 mmol
Acetic acid (90 %)	30 ml

Preparation carried out as for compound **4.13** to give an off white solid.

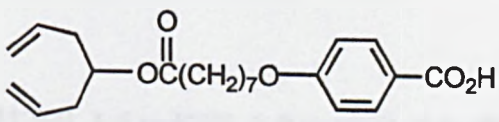
Yield = 1.68 g, 66 %.

IR ν_{max}(cm^{-1}): 770, 930, 1170, 1250, 1430, 1510, 1600, 1670, 1730, 2840, 2920, 3400.

^{1}H NMR: δ 1.4 m [6H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.15**

4-(hepta-1,6-dien-4-yloxycarbonylheptyloxy)benzoic acid



Compound **4.9** (505.4 g mol^{-1})	3.90 g, 7.72 mmol
Zinc powder (65.4 g mol^{-1})	5.05 g, 77.2 mmol
Acetic acid (90 %)	30 ml

Preparation carried out as for compound **4.13** to give an off white solid.

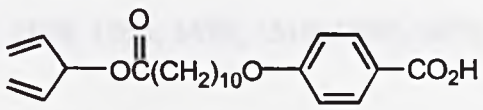
Yield = 2.04 g, 71 %.

IR $\nu_{max}(cm^{-1})$: 770, 930, 1170, 1250, 1430, 1510, 1600, 1670, 1730, 2840, 2920, 3400.

^1H NMR: δ 1.4 m [6H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 m [4H], 4.0 t [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.16**

4-(penta-1,4-dien-3-yloxycarbonyldecyloxy)benzoic acid



Compound **4.10** (519.4 g mol^{-1})	2.60 g, 5.01 mmol
Zinc powder (65.4 g mol^{-1})	3.28 g, 50.1 mmol
Acetic acid (90 %)	30 ml

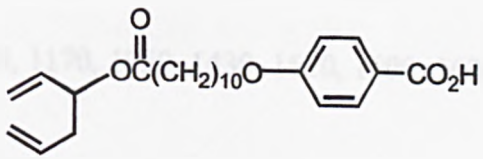
Preparation carried out as for compound **4.13** to give an off white solid.

Yield = 1.07 g, 55 %.

IR $\nu_{max}(cm^{-1})$: 770, 930, 1170, 1250, 1430, 1510, 1600, 1670, 1730, 2840, 2920, 3400.

^1H NMR: δ 1.4 m [12H], 1.6 m [2H], 1.9 m [2H], 2.4 t [2H], 4.0 t [2H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.17** 4-(hexa-1,5-dien-3-yloxycarbonyldecyloxy)benzoic acid



Compound **4.11** (533.4 g mol^{-1})	2.12 g, 3.97 mmol
Zinc powder (65.4 g mol^{-1})	2.60 g, 39.7 mmol
Acetic acid (90 %)	30 ml

Preparation carried out as for compound **4.13** to give an off white solid.

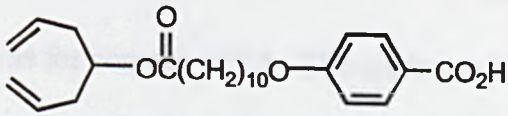
Yield = 0.88 g, 55 %.

IR $\nu_{max}(cm^{-1})$: 770, 930, 1170, 1250, 1430, 1510, 1600, 1670, 1730, 2840, 2920, 3400.

^1H NMR: δ 1.4 m [12H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 6.9 d [2H], 8.1 d[2H].

Compound **4.18**

4-(hepta-1,6-dien-4-yloxycarbonyldecyloxy)benzoic acid



Compound **4.12** (547.4 g mol^{-1})	2.67 g, 4.88 mmol
Zinc powder (65.4 g mol^{-1})	3.19 g, 48.8 mmol
Acetic acid (90 %)	30 ml

Preparation carried out as for compound **4.13** to give an off white solid.

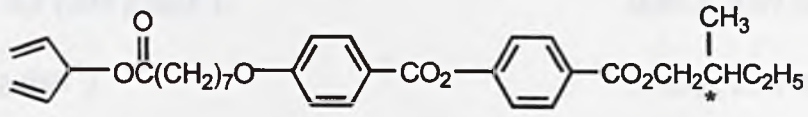
Yield = 0.87 g, 54 %.

IR $\nu_{max}(cm^{-1})$: 770, 930, 1170, 1250, 1430, 1510, 1600, 1670, 1730, 2840, 2920, 3400.

^1H NMR: δ 1.4 m [6H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 2.4 m [4H], 4.0 t [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 6.9 d [2H], 8.1 d [2H].

Compound **4.19**

(*S*)-2-Methylbutyl 4-[4-(penta-1,4-dien-3-yloxycarbonylheptyloxy)phenyl-cabonyloxy]benzoate



Compound **4.13** (329 g mol^{-1})	2.13 g, 6.47 mmol
Compound **4.3** (204 g mol^{-1})	1.32 g, 6.47 mmol
DCC (206 g mol^{-1})	1.46 g, 7.12 mmol
DMAP	Spatula tip
DCM (dry)	50 ml

Preparation carried out as for compound **1.1**. The crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* to give a colourless, viscous liquid.

Yield = 1.51 g, 45 %.

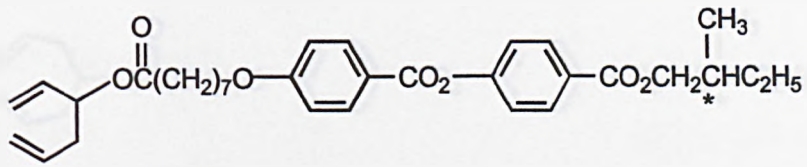
IR $\nu_{max}(cm^{-1})$: 720, 770, 1060, 1160, 1210, 1250, 1510, 1600, 1720, 2930.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [13H], 2.4 t [2H], 4.0 t [2H], 4.2 m [2H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 7.0 d [2H], 7.3 d [2H], 8.12 d [2H], 8.14 d [2H].

OR: $[\alpha]_D = +2.33°$.

Compound **4.20**

(*S*)-2-Methylbutyl 4-[4-(hexa-1,5-dien-3-yloxycarbonylheptyloxy)phenyl-cabonyloxy]benzoate



Compound **4.14** (360 g mol^{-1})	1.68 g, 4.67 mmol
Compound **4.3** (204 g mol^{-1})	0.95 g, 4.67 mmol
DCC (206 g mol^{-1})	1.06 g, 5.14 mmol
DMAP	Spatula tip
DCM (dry)	50 ml

Preparation carried out as for compound **1.1**. The crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* to give a colourless, viscous liquid.

Yield = 1.92g, 75 %.

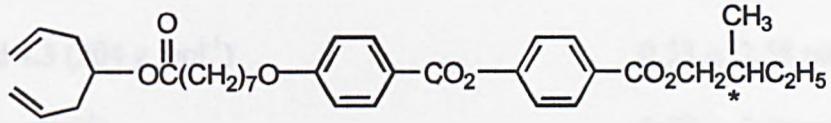
IR ν_{max}(cm^{-1}): 720, 770, 1060, 1160, 1210, 1250, 1510, 1600, 1720, 2930.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [13H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 4.2 m [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 7.0 d [2H], 7.3 d [2H], 8.12 d [2H], 8.14 d [2H].

OR: $[\alpha]_D$ = + 1.66°.

Compound **4.21**

(*S*)-2-Methylbutyl 4-[4-(hepta-1,6-dien-4-yloxycarbonylheptyloxy)phenyl-cabonyloxy]benzoate



Compound **4.15** (374 g mol^{-1})	2.04 g, 5.45 mmol
Compound **4.3** (204 g mol^{-1})	1.11 g, 5.45 mmol
DCC (206 g mol^{-1})	1.24 g, 6.00 mmol
DMAP	Spatula tip
DCM (dry)	50 ml

Preparation carried out as for compound **1.1**. The crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* to give a colourless, viscous liquid.

Yield = 1.13g, 37 %.

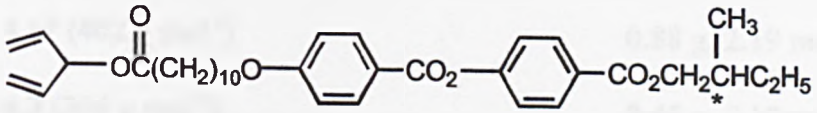
IR ν_{max}(cm^{-1}): 720, 770, 1060, 1160, 1210, 1250, 1510, 1600, 1720, 2930.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [13H], 2.3 t [2H], 2.4 t [4H], 4.0 t [2H], 4.2 m [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 7.0 d [2H], 7.3 d [2H], 8.12 d [2H], 8.14 d [2H].

OR: $[\alpha]_D = +2.64°$.

Compound **4.22**

(*S*)-2-Methylbutyl 4-[4-(penta-1,4-dien-3-yloxycarbonyldecyloxy)phenyl-cabonyloxy]benzoate



Compound **4.16** (388 g mol^{-1})	1.00 g, 2.58 mmol
Compound **4.3** (204 g mol^{-1})	0.53 g, 2.58 mmol
DCC (206 g mol^{-1})	0.59 g, 2.84 mmol
DMAP	Spatula tip
DCM (dry)	50 ml

Preparation carried out as for compound **1.1**. The crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* to give a white, waxy solid.

Yield = 1.13 g, 79 %.

IR $\nu_{max}(cm^{-1})$: 720, 770, 1060, 1160, 1210, 1250, 1510, 1600, 1720, 2930.

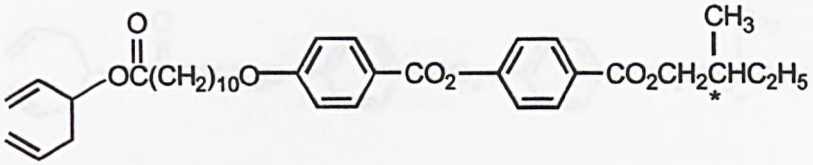
^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [19H], 2.4 t [2H], 4.0 t [2H], 4.2 m [2H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 7.0 d [2H], 7.3 d [2H], 8.12 d [2H], 8.14 d [2H].

OR: $[\alpha]_D = +1.70°$.

Compound **4.23**

(*S*)-2-Methylbutyl 4-[4-(hexa-1,5-dien-3-yloxycarbonyldecyloxy)phenyl-

cabonyloxy]benzoate



Compound **4.17** (402 g mol^{-1})	0.88 g, 2.19 mmol
Compound **4.3** (204 g mol^{-1})	0.45 g, 2.19 mmol
DCC (206 g mol^{-1})	0.50 g, 2.41 mmol
DMAP	Spatula tip
DCM (dry)	50 ml

Preparation carried out as for compound **1.1**. The crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* to give a white, waxy solid.

Yield = 1.18 g, 91 %.

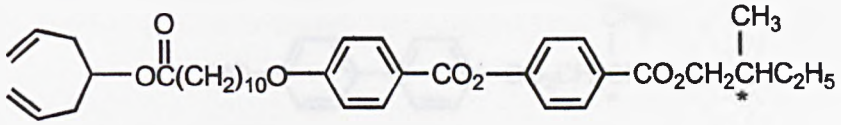
IR ν_{max}(cm^{-1}): 720, 770, 1060, 1160, 1210, 1250, 1510, 1600, 1720, 2930.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [19H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 4.2 m [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 7.0 d [2H], 7.3 d [2H], 8.12 d [2H], 8.14 d [2H].

OR: $[\alpha]_D$ = + 1.62°.

Compound **4.24**

(*S*)-2-Methylbutyl 4-[4-(hepta-1,6-dien-4-yloxycarbonylheptyloxy)phenyl-cabonyloxy]benzoate



Compound **4.13** (416 g mol^{-1})	0.87 g, 2.09 mmol
Compound **4.3** (204 g mol^{-1})	0.43 g, 2.09 mmol
DCC (206 g mol^{-1})	0.47 g, 2.30 mmol
DMAP	Spatula tip
DCM (dry)	50 ml

Preparation carried out as for compound **1.1**. The crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* to give a white, waxy solid.

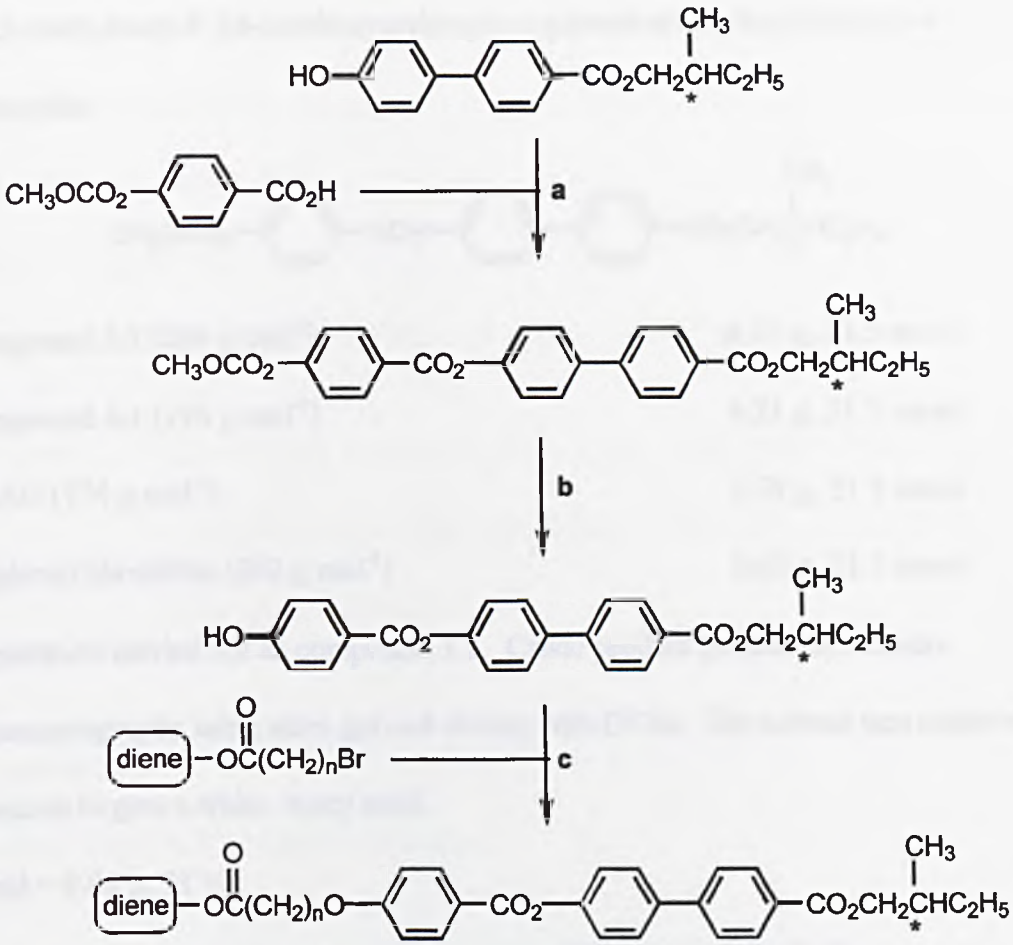
Yield = 1.10 g, 87 %.

IR ν_{max}(cm^{-1}): 720, 770, 1060, 1160, 1210, 1250, 1510, 1600, 1720, 2930.

^{1}H NMR: δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 u [19H], 2.3 t [2H], 2.4 t [4H], 4.0 t [2H], 4.2 m [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 7.0 d [2H], 7.3 d [2H], 8.12 d [2H], 8.14 d [2H].

OR: $[\alpha]_D$ = + 1.36°.

2.4.5 Series 5



Scheme **5**

a (*S*)-(-)-2-Methylbutan-1-ol, DEAD, triphenylphosphine, THF (dry).

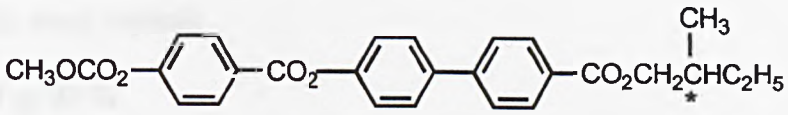
b **d** 0.880 ammonia (aq.), ethanol, THF.

c Potassium carbonate (dry), butanone (dry).

Synthesis Of Compounds From Scheme 5

Compound **5.1**

(*S*)-2-Methylbutyl 4'-[4-(methoxycarbonyloxy)phenylcarbonyloxy]biphenyl-4-carboxylate



Compound **3.2** (284 g mol^{-1})	6.11 g, 21.5 mmol
Compound **4.1** (196 g mol^{-1})	4.21 g, 21.5 mmol
DEAD (174 g mol^{-1})	3.74 g, 21.5 mmol
Triphenyl phosphine (262 g mol^{-1})	5.63 g, 21.5 mmol

Preparation carried out as compound **3.2**. Crude product purified by column chromoatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* to give a white, waxy solid.

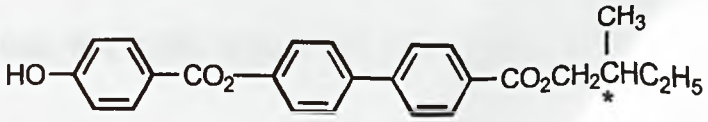
Yield = 9.08 g, 91 %.

IR ν_{max}(cm^{-1}): 780, 1170, 1260, 1440, 1600, 1710, 1730,1750, 2960.

^{1}H NMR δ 0.95 d [3H], 1.02 t [3H], 1.2 m [1H], 1.6 m [1H], 1.9 m [1H], 3.95 s [3H], 4.2 m [2H], 7.32 d [2H], 7.36 d [2H], 7.66 d [2H], 7.68 d [2H], 8.13 d [2H], 8.28 d [2H].

Compound **5.2**

(*S*)-2-Methylbutyl 4'-(4-hydroxyphenylcarbonyloxy)biphenyl-4-carboxylate



Compound **5.1** (462 g mol^{-1})	9.08 g, 19.6 mmol
Ethanol	100 ml
THF	100 ml
d 0.880 Ammonia solution	50 ml

Preparation carried out as compound **3.3.** Crude product recrystallised from ethanol to give white, waxy crystals.

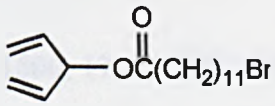
Yield = 7.67 g, 93 %.

IR ν_{max}(cm^{-1}): 780, 1170, 1260,1500,1580, 1600, 1690,1700, 2960, 3400.

^{1}H NMR δ 0.95 d [3H], 1.02 t [3H], 1.2 m [1H], 1.6 m [1H], 1.9 m [1H], 4.2 m [2H], 7.32 d [2H], 7.36 d [2H], 7.66 d [2H], 7.68 d [2H], 8.13 d [2H], 8.28 d [2H].

Compound **5.3**

Penta-1,4-dien-3-yl 12-bromododecanoate



Penta-1,4-dien-3-ol (84 g mol^{-1})	0.90 g, 10.72 mmol
12-Bromododecanoic acid (279 g mol^{-1})	3.00 g, 10.72 mmol
DCC (206 g mol^{-1})	2.32 g, 11.3 mmol
DMAP	Spatula tip

Preparation carried out as for compound **1.1**, to give a colourless, viscous liquid.

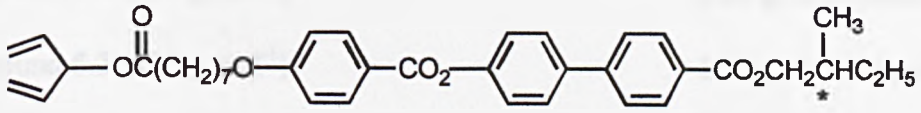
Yield = 2.89 g, 81 %.

IR ν_{max}(cm^{-1}): 930, 980, 1240, 1640, 1730, 2850, 2920.

^{1}H NMR δ 1.3 m [14H], 1.6 m [2H], 1.9 m [2H], 2.3 t [2H], 3.4 t [2H], 5.30 m [4H], 5.7 t [1H], 5.80 m [2H].

Compound **5.4**

(*S*)-2-Methylbutyl 4'-[4-(penta-1,4-dien-3-yloxycarbonylheptyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **3.3** (289 g mol^{-1})	1.03 g, 3.57 mmol
Compound **5.2** (420 g mol^{-1})	1.50 g, 3.57 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.09 g, 49 %.

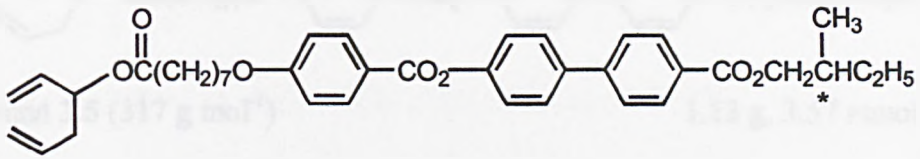
IR ν_{max}(cm^{-1}): 780, 1170, 1260, 1600, 1710, 1730, 2850, 2920.

^{1}H NMR δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [13H], 2.3 t [2H], 4.0 t [2H], 4.2 m [2H], 5.30 m [4H], 5.7 t [1H], 5.80 m [2H], 7.0 d [2H], 7.3 d [2H], 7.7 m [4H], 8.12 d [2H], 8.15 d [2H].

OR $[\alpha]_D$ = + 5.41°.

Compound **5.5**

(*S*)-2-Methylbutyl 4'-[4-(hexa-1,5-dien-3-yloxycarbonylheptyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **3.4** (303 g mol^{-1})	1.08 g, 3.57 mmol
Compound **5.2** (420 g mol^{-1})	1.50 g, 3.57 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.29 g, 56 %.

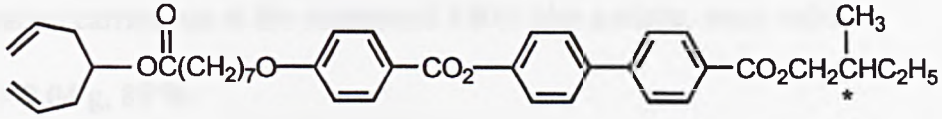
IR ν_{max}(cm^{-1}): 780, 1170, 1260, 1600, 1710, 1730, 2850, 2920.

^{1}H NMR δ 0.95 d[3H], 1.02 t [3H], 1.1-2.0 m [13H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 4.2 m [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 7.0 d [2H], 7.3 d [2H], 7.7 m [4H], 8.12 d [2H], 8.15 d [2H].

OR $[\alpha]_D$ = + 2.92°.

Compound **5.6**

(*S*)-2-Methylbutyl 4'-[4-(hepta-1,6-dien-4-yloxycarbonylheptyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **3.5** (317 g mol^{-1})	1.13 g, 3.57 mmol
Compound **5.2** (420 g mol^{-1})	1.50 g, 3.57 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.43 g, 61 %.

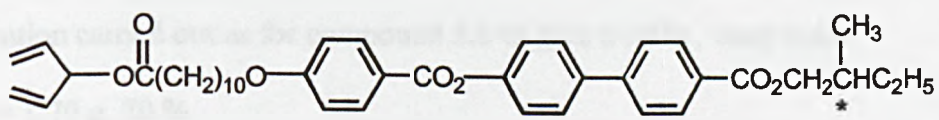
IR ν_{max}(cm^{-1}): 780, 1170, 1260, 1600, 1710, 1730, 2850, 2920.

^{1}H NMR δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [13H], 2.3 t [2H], 2.4 m[4H], 4.0 t [2H], 4.2 m [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 7.0 d [2H], 7.3 d [2H], 7.7 m [4H], 8.12 d [2H], 8.15 d [2H].

OR $[\alpha]_D$ = + 1.63°.

Compound **5.7**

(*S*)-2-Methylbutyl 4'-[4-(penta-1,4-dien-3-yloxycarbonyldecyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **2.1** (331 g mol^{-1})	1.20 g, 3.57 mmol

Compound **5.2** (420 g mol^{-1})	1.50 g, 3.57 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 2.04 g, 85 %.

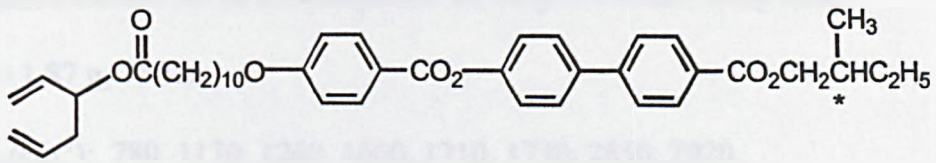
IR ν_{max}(cm^{-1}): 780, 1170, 1260, 1600, 1710, 1730, 2850, 2920.

^{1}H NMR δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [19H], 2.3 t [2H], 4.0 t [2H], 4.2 m [2H], 5.30 m [4H], 5.7 t [1H], 5.80 m [2H], 7.0 d [2H], 7.3 d [2H], 7.7 m [4H], 8.12 d [2H], 8.15 d [2H].

OR $[\alpha]_D = +1.86°$.

Compound **5.8**

(*S*)-2-Methylbutyl 4'-[4-(hexa-1,5-dien-3-yloxycarbonyldecyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **2.2** (345 g mol^{-1})	1.23 g, 3.57 mmol
Compound **5.2** (420 g mol^{-1})	1.50 g, 3.57 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.70 g, 70 %.

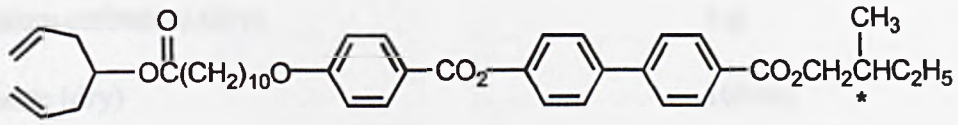
IR ν_{max}(cm^{-1}): 780, 1170, 1260, 1600, 1710, 1730, 2850, 2920.

^{1}H NMR δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [19H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 4.2 m [2H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 7.0 d [2H], 7.3 d [2H], 7.7 m [4H], 8.12 d [2H], 8.15 d [2H].

OR $[\alpha]_D = +1.19°$.

Compound **5.9**

(*S*)-2-Methylbutyl 4'-[4-(hepta-1,6-dien-4-yloxycarbonyldecyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **2.3** (359 g mol^{-1})	1.30 g, 3.57 mmol
Compound **5.2** (420 g mol^{-1})	1.50 g, 3.57 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.87 g, 75 %.

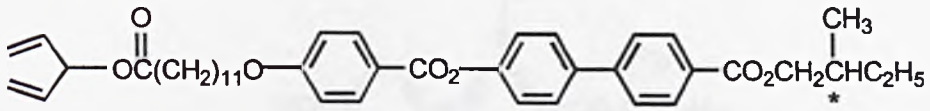
IR ν_{max}(cm^{-1}): 780, 1170, 1260, 1600, 1710, 1730, 2850, 2920.

^{1}H NMR δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [19H], 2.3 t [2H], 2.4 m [4H], 4.0 t [2H], 4.2 m [2H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 7.0 d [2H], 7.3 d [2H], 7.7 m [4H], 8.12 d [2H], 8.15 d [2H].

OR $[\alpha]_D = +2.36°$.

Compound **5.10**

(*S*)-2-Methylbutyl 4'-[4-(penta-1,4-dien-3-yloxycarbonylundecyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **5.3** (345 g mol^{-1})	1.65 g, 4.78 mmol
Compound **5.2** (420 g mol^{-1})	2.01 g, 4.78 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

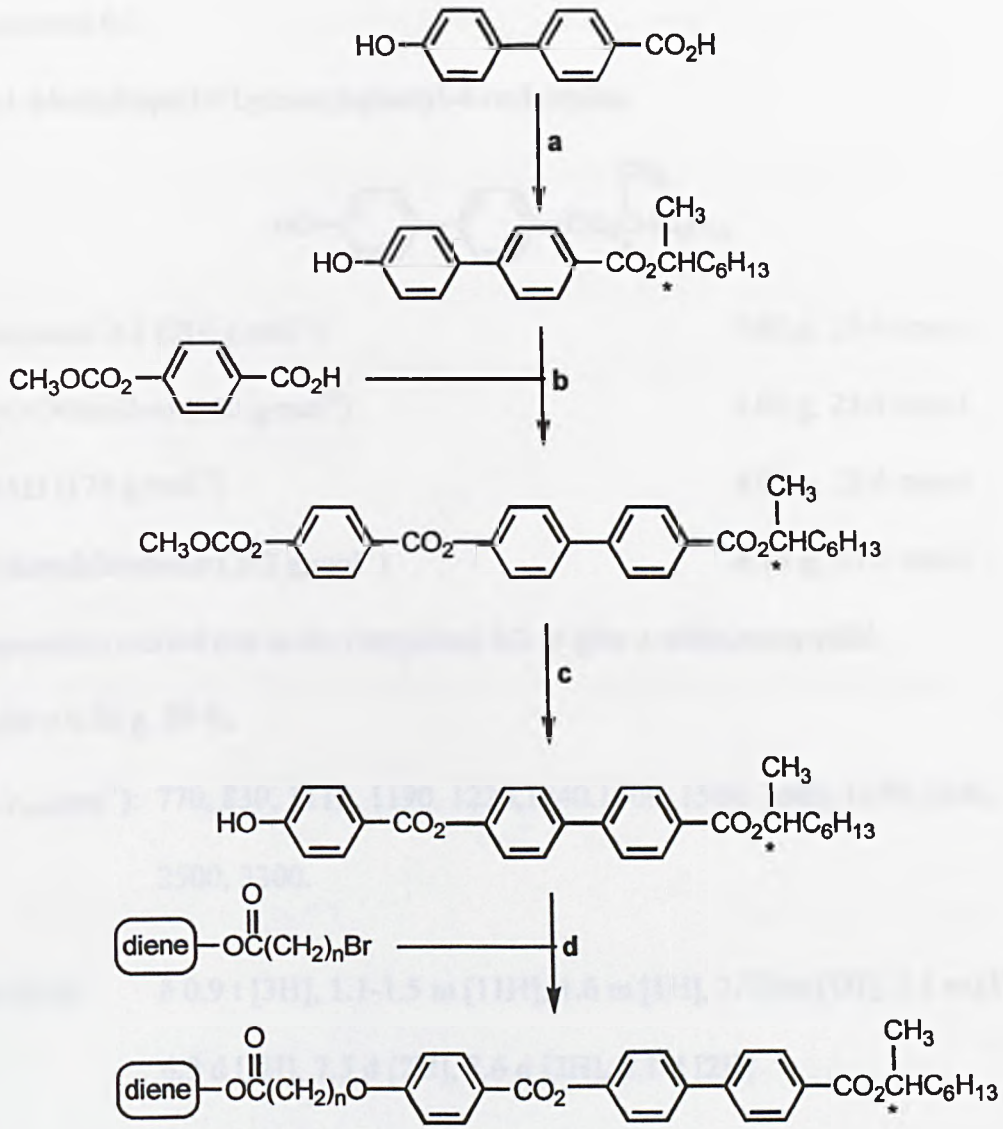
Yield = 2.51 g, 77 %.

IR ν_{max}(cm^{-1}): 780, 1170, 1260, 1600, 1710, 1730, 2850, 2920.

^{1}H NMR δ 0.95 d [3H], 1.02 t [3H], 1.1-2.0 m [21H], 2.3 t [2H], 4.0 t [2H], 4.2 m [2H], 5.30 m [4H], 5.7 t [1H], 5.80 m [2H], 7.0 d [2H], 7.3 d [2H], 7.7 m [4H], 8.12 d [2H], 8.15 d [2H].

OR $[\alpha]_D = +3.14°$.

2.4.6 Series 6



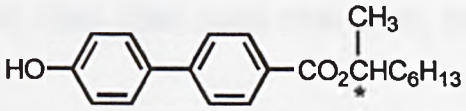
Scheme 6

a	(*S*)-(+)-octan-2-ol, DEAD, triphenylphosphine, THF (dry).
b	DEAD, triphenylphosphine, THF (dry).
c	**d** 0.880 ammonia (aq.), ethanol, THF.
d	Potassium carbonate (dry), butanone (dry).

Synthesis Of Compounds From Scheme 6

Compound **6.1**

(*R*)-1-Methylheptyl 4'hydroxybiphenyl-4-carboxylate



Compound **3.1** (214 g mol^{-1})	5.00 g, 23.4 mmol
S-(+)-Octan-2-ol (130 g mol^{-1})	3.04 g, 23.4 mmol
DEAD (174 g mol^{-1})	4.07 g, 23.4 mmol
Triphenylphosphine (262 g mol^{-1})	6.13 g, 23.4 mmol

Preparation carried out as for compound **3.2** to give a white,waxy solid.

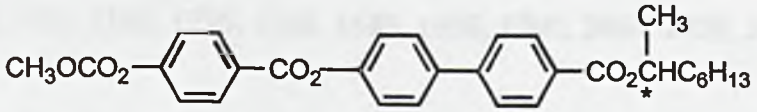
Yield = 6.80 g, 89 %.

IR ν_{max}(cm^{-1}): 770, 830, 1110, 1190, 1220,1240,1500, 1580, 1600, 1670, 2840, 2500, 3300.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [11H], 1.6 m [1H], 1.75 m [1H], 5.1 m [1H], 6.9 d [2H], 7.5 d [2H], 7.6 d [2H], 8.1 d [2H].

Compound **6.2**

(*R*)-1-Methylheptyl 4'-[4-(methoxycarbonyloxy)phenylcarbonyloxy]biphenyl-4-carboxylate



Compound **6.1** (326 g mol^{-1})	6.17 g, 18.9 mmol
Compound **4.1** (196 g mol^{-1})	3.70 g, 18.9 mmol

DEAD (174 g mol^{-1}) 3.29 g, 18.9 mmol

Triphenylphosphine (262 g mol^{-1}) 4.95 g, 18.9 mmol

Preparation carried out as for compound **3.2**, to give a white, waxy solid.

Yield = 4.77 g, 50 %.

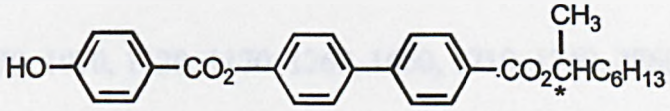
IR ν_{max}(cm^{-1}): 770, 1100, 1220, 1260, 1440, 1700, 1720, 1750, 2860, 2920, 2950.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [11H], 1.6 m [1H], 1.75 m [1H], 4.0 s [3H], 5.1 m [1H], 6.9 d [2H], 7.3 d [2H], 7.65 m [4H], 8.1 m [4H].

OR: $[\alpha]_D$ = - 28.09°.

Compound **6.3**

(*R*)-1-Methylheptyl 4'-(4-hydroxyphenylcarbonyloxy)biphenyl-4-carboxylate



Compound **6.2** (504 g mol^{-1}) 4.77 g, 9.46 mmol

Ethanol 100 ml

THF 100 ml

d0.880 Ammonia solution 50 ml

Preparation carried out as for compound **3.3**. Crude product recrystallised from ethanol to give white, waxy crystals.

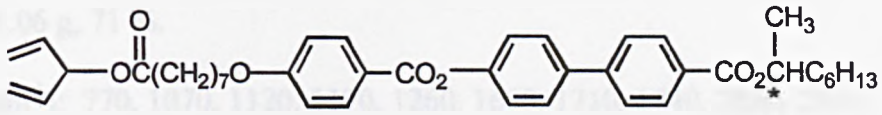
Yield = 4.11 g, 88 %.

IR ν_{max}(cm^{-1}): 770, 1160, 1270, 1500, 1580, 1600, 1700, 2860, 2920, 3400.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [11H], 1.6 m [1H], 1.75 m [1H], 5.1 m [1H], 6.9 d [2H], 7.3 d [2H], 7.65 m [4H], 8.1 m [4H].

Compound **6.4**

(*R*)-1-Methylheptyl 4'-[4-(penta-1,4-dien-3-yloxycarbonylheptyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **6.3** (490 g mol^{-1}) 2.50 g, 5.10 mmol

Compound **3.3** (289 g mol^{-1}) 1.47 g, 5.10 mmol

Potassium carbonate (dry) 5 g

Butanone (dry) 100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.82 g, 51 %.

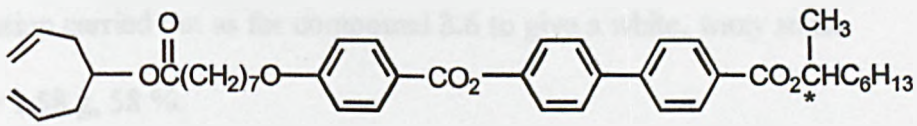
IR ν_{max}(cm^{-1}): 770, 1070, 1120, 1170, 1260, 1600, 1710, 1740, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [21H], 1.6 m [1H], 1.75 m [1H], 2.3 t [2H], 4.0 t [2H], 5.1 m [1H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 7.3 d [2H], 7.65 m [4H], 8.1 m [4H].

OR: $[\alpha]_D$ = - 24.65°.

Compound **6.5**

(*R*)-1-Methylheptyl 4'-[4-(hepta-1,6-diene-4-yloxycarbonylheptyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **6.3** (490 g mol^{-1}) 1.00 g, 2.07 mmol

Compound **3.5** (317 g mol^{-1})	0.65 g, 2.07 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.06 g, 71 %.

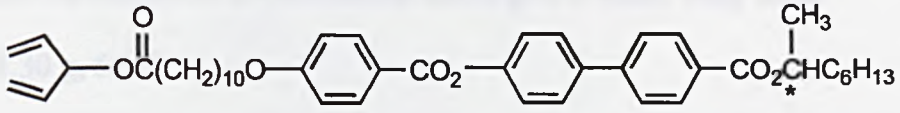
IR ν_{max}(cm^{-1}): 770, 1070, 1120, 1170, 1260, 1600, 1710, 1740, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [21H], 1.6 m [1H], 1.75 m [1H], 2.3 t [2H], 2.4 t [4H], 4.0 t [2H], 5.0 quint [1H], 5.1 m [5H], 5.75 m [2H], 6.9 d [2H], 7.3 d [2H], 7.65 m [4H], 8.1 m [4H].

OR: $[\alpha]_D$ = - 21.07°.

Compound **6.6**

(*R*)-1-Methylheptyl 4'-[4-(penta-1,4-dien-3-yloxycarbonyldecyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **6.3** (490 g mol^{-1})	1.50 g, 3.10 mmol
Compound **2.1** (331 g mol^{-1})	1.03 g, 3.10 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.58 g, 58 %.

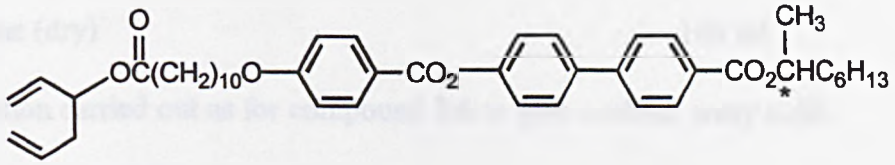
IR ν_{max}(cm^{-1}): 770, 1070, 1120, 1170, 1260, 1600, 1710, 1740, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [27H], 1.6 m [1H], 1.75 m [1H], 2.3 t [2H], 4.0 t [2H], 5.1 m [1H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 7.3 d [2H], 7.65 m [4H], 8.1 m [4H].

OR: $[\alpha]_D$ = - 22.08°.

Compound **6.7**

(*R*)-1-Methylheptyl 4'-[4-(hexa-1,5-diene-3-yloxycarbonyldecyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **6.3** (490 g mol^{-1})	1.50 g, 3.10 mmol
Compound **2.2** (345 g mol^{-1})	1.07 g, 3.10 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.30 g, 56 %.

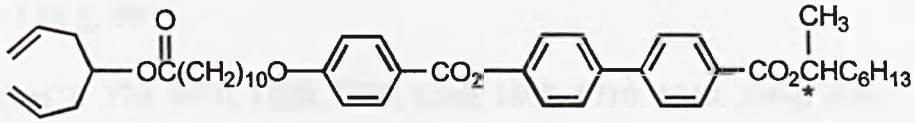
IR ν_{max}(cm^{-1}): 770, 1070, 1120, 1170, 1260, 1600, 1710, 1740, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [27H], 1.6 m [1H], 1.75 m [1H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 5.1 m [1H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], 6.9 d [2H], 7.3 d [2H], 7.65 m [4H], 8.1 m [4H].

OR: $[\alpha]_D$ = - 26.13°.

Compound **6.8**

(*R*)-1-Methylheptyl 4'-[4-(hepta-1,6-diene-4-yloxycarbonyldecyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **6.3** (490 g mol^{-1})	2.00 g, 4.08 mmol
Compound **3.3** (289 g mol^{-1})	1.46 g, 4.08 mmol
Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 1.51 g, 48 %.

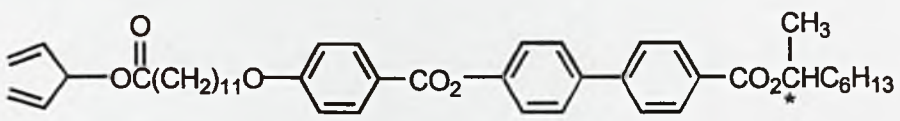
IR ν_{max}(cm^{-1}): 770, 1070, 1120, 1170, 1260, 1600, 1710, 1740, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [27H], 1.6 m [1H], 1.75 m [1H], 2.3 t [2H], 2.4 t [4H], 4.0 t [2H], 5.0 quint [1H], 5.1 m [5H], 5.75 m [2H], 6.9 d [2H], 7.3 d [2H], 7.65 m [4H], 8.1 m [4H].

OR: $[\alpha]_D$ = - 25.00°.

Compound **6.9**

(*R*)-1-Methylheptyl 4'-[4-(penta-1,4-dien-3-yloxycarbonyldecyloxy)phenyl-carbonyloxy]biphenyl-4-carboxylate



Compound **6.3** (490 g mol^{-1})	2.00 g, 3.08 mmol
Compound **5.3** (345 g mol^{-1})	1.41 g, 3.08 mmol

Potassium carbonate (dry)	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

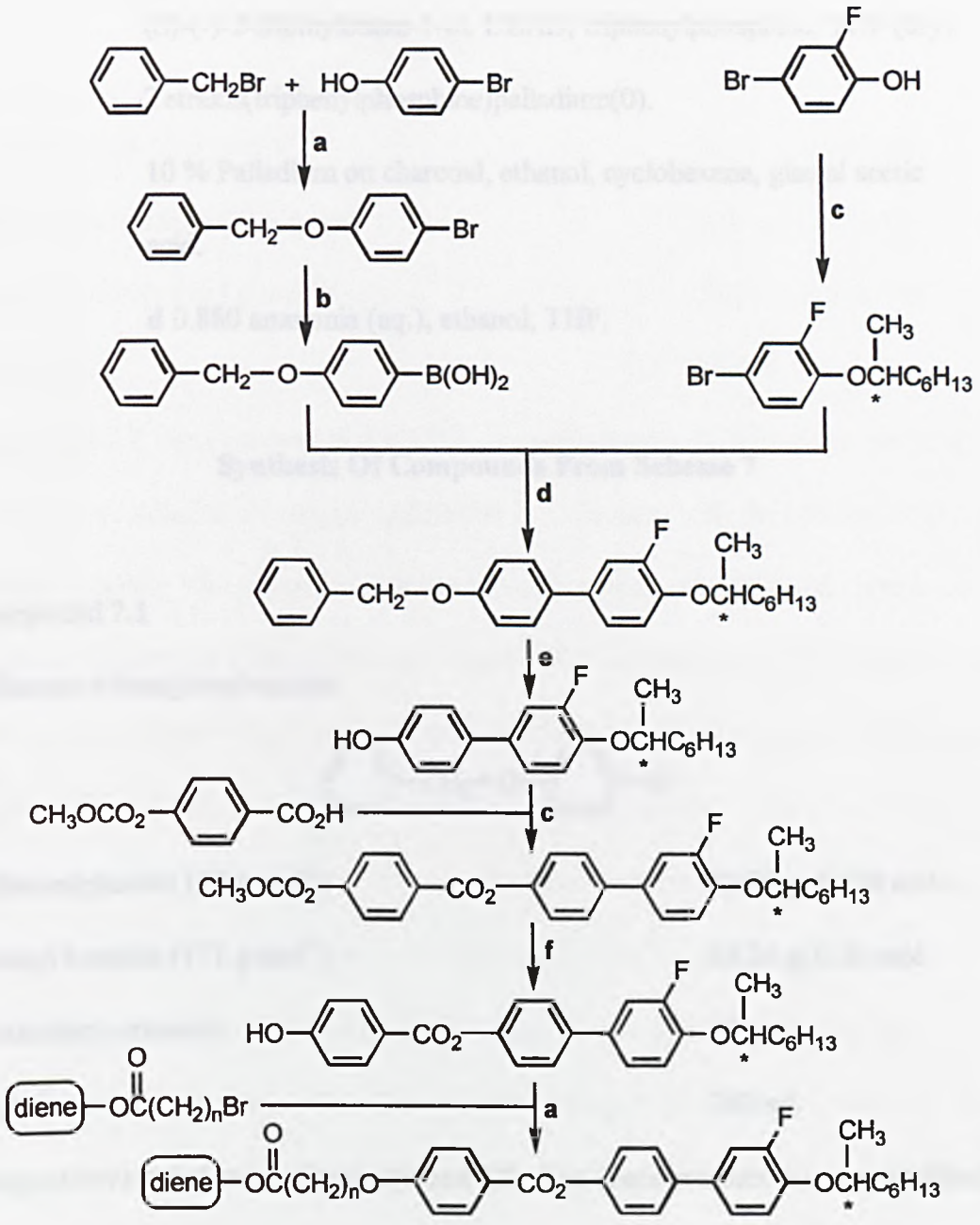
Yield = 1.84 g, 60 %.

IR $\nu_{max}(cm^{-1})$: 770, 1070, 1120, 1170, 1260, 1600, 1710, 1740, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.1-1.5 m [29H], 1.6 m [1H], 1.75 m [1H], 2.3 t [2H], 4.0 t [2H], 5.1 m [1H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 7.3 d [2H], 7.65 m [4H], 8.1 m [4H].

OR: $[\alpha]_D$ = - 22.77°.

2.4.7 Series 7



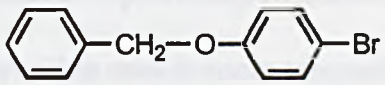
Scheme 7

a	Potassium carbonate (dry), butanone (dry).
b	**i)** Magnesium turnings, THF (dry), **ii)** trimethyl borate, **iii)** hydrochloric acid
c	(*S*)-(-)-2-Methylbutan-1-ol, DEAD, triphenylphosphine, THF (dry).
d	Tetrakis(triphenylphosphine)palladium(0).
e	10 % Palladium on charcoal, ethanol, cyclohexene, glacial acetic acid.
f	**d** 0.880 ammonia (aq.), ethanol, THF.

Synthesis Of Compounds From Scheme 7

Compound **7.1**

1-Bromo-4-benzyloxybenzene



4-Bromophenol (173 g mol^{-1})	25.95 g, 0.150 mol
Benzyl bromide (171 g mol^{-1})	34.20 g, 0.20 mol
Potassium carbonate	50 g
Butanone	200 ml

Preparation carried out as for compound **1.2**. The crude product was recrystallised from ethanol and dried *in vacuo* to yield a white, crystalline solid.

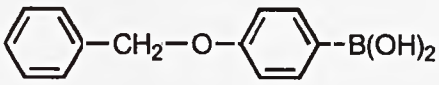
Yield = 33.06 g, 84 %.

IR ν_{max}(cm^{-1}): 730, 820, 1240, 1450, 1480, 2570, 1580, 2480.

^{1}H NMR: δ 5.0 s [2H], 6.8 d [2H], 7.4 m [7H].

Compound **7.2**

4-Benzyloxyphenylboronic acid



Compound **7.1** (263 g mol^{-1})	70.91 g, 0.270 mol
Magnesium turnings (24.3 g mol^{-1})	7.21 g, 0.297 mol
Trimethyl borate (104 g mol^{-1})	56.11 g, 0.540 mol
THF (dry)	250 ml

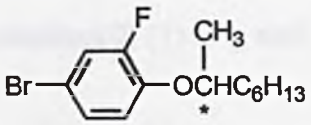
Compound **7.1** was dissolved in dry THF. A small amount (30 ml) of the resulting solution was added to the magnesium, under dry nitrogen, with the addition of a crystal of iodine. The mixture was heated to reflux, upon which reaction commenced. The remainder of the THF solution of compound **7.1** was then added at such a rate as that a gentle reflux was maintaned. Upon complete addition the reaction was heated under reflux for 1 h, then allowed to cool to room temperature. The reaction was then cooled (0 °C) and trimethyl borate was added dropwise with vigorous stirring. After complete addition the reaction was stirred for 3 h, then hydrochloric acid (10 %, 200 ml) was added slowly, then left to stir overnight. The product was extracted into di-ethyl ether (2 × 500 ml), then washed with water (2 × 500 ml). The product was then extracted into potassium hydroxide solution (10 %, 2 × 500 ml). The combined aqueous extract was acidified with concentrated hydrochloric acid, until no further preciptation occured. The precipitate was filtered off and dissolved in di-ethyl ether (250 ml) and washed with water (2 × 250 ml). The organic phase was

dried with magnesium sulphate and the solvent was removed *in vacuo* to give an off white, powder. The product was used without analysis.

Yield = 36.74 g, 60 %.

Compound **7.3**

(*R*)-4-Bromo-2-fluoro-1-(1-methylheptyloxy)benzene



4-Bromo-2-fluorophenol (191 g mol^{-1})	25.00 g, 0.131 mol
S-(+)-octan-2-ol (130 g mol^{-1})	17.02 g, 0.131 mol
DEAD (174 g mol^{-1})	22.79 g, 0.131 mol
Triphenylphosphine (262 g mol^{-1})	34.32 g, 0131 mol
THF (dry)	250 ml

Preparation carried out as for compound **3.2**. The crude compound was purified by column chromatography using silica gel and eluting with petrol (b.p. 40-60 °C). The solvent was removed *in vacuo* to give a colourless liquid.

Yield = 32.49 g, 82 %.

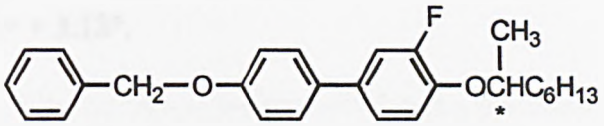
IR ν_{max}(cm^{-1}): 850, 1130, 1200, 1260, 1490, 1580, 2350, 3420.

^{1}H NMR: δ 0.9 t [3H], 1.2-1.5 m [11H], 1.56 m [1H], 1.73 m [1H], 4.3 m [1H], 6.83 t [1H], 7.15 m [1H], 7.21 dd [1H].

OR: $[\alpha]_D$ = -2.55°.

Compound **7.4**

(*R*)-4'-Benzyloxy-3-fluoro-4-(1-methylheptyloxy)biphenyl -



Compound **7.2** (161 g mol^{-1})	26.40 g, 0.116 mol
Compound **7.3** (228 g mol^{-1})	31.90 g, 0.105 mol
Tetrakis(triphenylphosphine)palladium(0) (1155 g mol^{-1})	6.10 g, 5.25 mmol
DME	300 ml
2M Sodium carbonate (aq.)	200 ml

Compound **7.3** was dissolved in DME (100 ml) and added to the 2M sodium carbonate solution. The mixture was heated to reflux, with stirring, under dry nitrogen. Then the tetrakis(triphenylphosphine)palladium(0) was added in one portion and a solution of compound **7.2** in DME (200 ml) was added dropwise. After complete addition the mixture was left heating under reflux overnight and was then allowed to cool to room temperature. The mixture was extracted with di-ethyl ether (2 x 200 ml), then the combined organic extracts were washed with brine (200 ml) and dried with magnesium sulphate. The solvent was removed *in vacuo* and the crude product was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo* and the resulting solid was recrystallised from petrol (b.p. 40-60 °C) and dried *in vacuo* to give white waxy plate like crystals.

Yield = 33.78 g, 79 %.

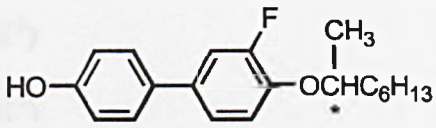
IR ν_{max}(cm^{-1}): 740, 800, 1050, 1240, 1280, 1500, 1610.

^{1}H NMR: δ 0.9 t [3H], 1.2-1.5 m [11H], 1.56 m [1H], 1.73 m [1H], 4.3m[1H], 5.0 s [2H], 7.0 m [3H], 7.25 m [2H], 7.4 m [7H].

OR: $[\alpha]_D = +3.13°$.

Compound **7.5**

(*R*)-3-Fluoro-4'-hydroxy-4-(1-methylheptyloxy)biphenyl [2]



Compound **7.4** (406 g mol^{-1})	33.70 g, 83 mmol
Palladium on charcoal (10 %)	0.50 g
Ethanol	600 ml
Glacial acetic acid	60 ml
Cyclohexene (82 g mol^{-1})	13.60 g, 0.167 mol

All the reactants and reagents were combined and heated, with stirring, under reflux until completion (TLC, ≈ 48 h). The mixture was allowed to cool to room temperature and the palladium on charcoal was filtered off. The solvent was removed *in vacuo* to yield a pale yellow oil. The crude product was purified by column chromatography using silica gel and eluting with DCM and then with ethyl acetate / petrol (b.p. 40-60 °C) (1:1). The solvent was removed *in vacuo* to give a white, waxy solid.

Yield = 26.01 g, 99 %.

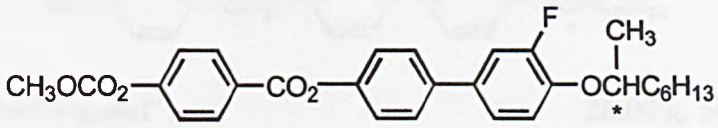
IR ν_{max}(cm^{-1}): 830, 1140, 1240, 1500, 1610, 2860, 2940, 3400.

^{1}H NMR: δ 0.9 t [3H], 1.2-1.5 m [11H], 1.56 m [1H], 1.73 m [1H], 4.3m [1H], 6.9 d [2H], 7.0 t [1H], 7.20 m [1H], 7.25 dd [1H], 7.4 d [2H].

OR: $[\alpha]_D = +3.94°$.

Compound **7.6**

(*R*)-3-Fluoro-4-(1-methylheptyloxy)biphenyl-4'-yl 4-(methoxycarbonyloxy)benzoate



Compound **7.5** (315 g mol^{-1})	26.00 g, 82.5 mmol
Compound **4.2** (196 g mol^{-1})	16.17 g, 82.5 mmol
DEAD (174 g mol^{-1})	14.34 g, 82.5 mmol
Triphenylphosphine (262 g mol^{-1})	21.62 g, 82.5 mmol

Preparation carried out as for compound **3.2**. The crude compound was purified by column chromatography using silica gel and eluting with DCM. The solvent was removed *in vacuo*, the solid was recrystallised from ethanol and dried *in vacuo* to give a white, waxy solid.

Yield = 28.30 g, 70 %.

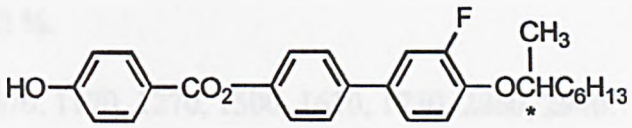
IR $\nu_{max}(cm^{-1})$: 800, 1260, 1500, 1610, 1730, 1760, 2860, 2940.

^1H NMR: δ 0.9 t [3H], 1.2-1.5 m [11H], 1.56 m [1H], 1.73 m [1H], 4.0 s [2H], 4.3 m [1H], 7.0 t [1H], 7.30 m [6H], 7.6 d [2H], 8.3 d [2H].

OR: $[\alpha]_D = +3.18°$.

Compound **7.7**

(*R*)-3-Fluoro-4-(1-methylheptyloxy)biphenyl-4'-yl 4-hydroxybenzoate



Compound **7.6** (493 g mol^{-1})	28.00 g, 56.8 mmol
Ethanol	100 ml
THF	100 ml
d 0.880 Ammonia (aq.)	50 ml

Preparation carried out as for compound **4.3**. The crude product was recrystallised from ethanol and dried *in vacuo* to give a white, crystalline solid.

Yield = 18.63 g, 75 %.

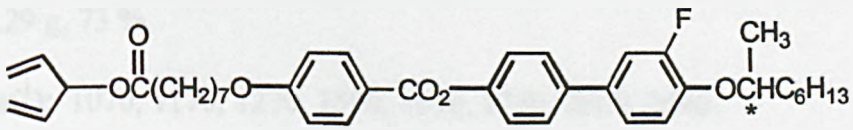
IR ν_{max}(cm^{-1}): 1160, 1210, 1280, 1510, 1590, 1610, 1700, 2860, 2940, 3400.

^{1}H NMR: δ 0.9 t [3H], 1.2-1.5 m [11H], 1.56 m [1H], 1.73 m [1H], 4.3 m [1H], 6.9 d [2H], 7.0 t [1H], 7.30 m [4H], 7.6 d [2H], 8.2 d [2H].

OR: $[\alpha]_D = +4.62°$.

Compound **7.8**

(*R*)-3-Fluoro-4-(1-methylheptyloxy)biphenyl-4'-yl 4-(penta-1,4-dien-3-yloxycarbonylheptyloxy)benzoate



Compound **7.7** (435 g mol^{-1})	2.00 g, 4.60 mmol
Compound **3.3** (289 g mol^{-1})	1.33 g, 4.60 mmol

Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 2.42 g, 82 %.

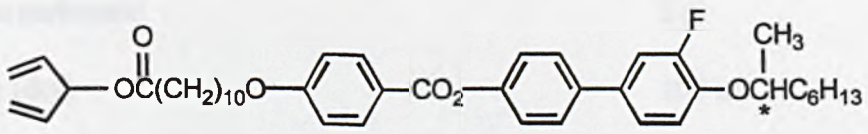
IR $\nu_{max}(cm^{-1})$: 1070, 1170, 1270, 1500, 1610, 1730, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.2-1.5 m [27H], 1.56 m [1H], 1.73 m [1H], 2.3 t [2H], 4.0 t [2H], 4.3m [1H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 7.0 t [1H], 7.30 m [4H], 7.6 d [2H], 8.2 d [2H].

OR: $[\alpha]_D = +1.02°$.

Compound **7.9**

(*R*)-3-Fluoro-4-(1-methylheptyloxy)biphenyl-4'-yl 4-(penta-1,4-dien-3-yloxycarbonyldecyloxy)benzoate



Compound **7.7** (435 g mol^{-1})	2.00 g, 4.60 mmol
Compound **2.1** (331 g mol^{-1})	1.52 g, 4.60 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 2.29 g, 73 %.

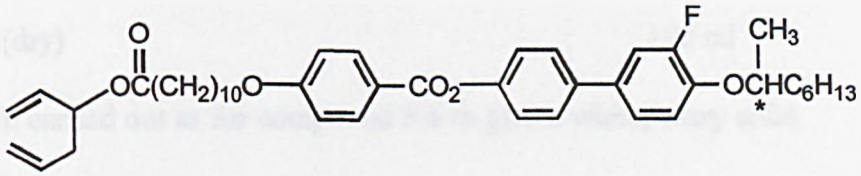
IR $\nu_{max}(cm^{-1})$: 1070, 1170, 1270, 1500, 1610, 1730, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.2-1.5 m [27H], 1.56 m [1H], 1.73 m [1H], 2.3 t [2H], 4.0 t [2H], 4.3 m [1H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 7.0 t [1H], 7.30 m [4H], 7.6 d [2H], 8.2 d [2H].

OR: $[\alpha]_D = +1.71°$.

Compound **7.10**

(*R*)-3-Fluoro-4-(1-methylheptyloxy)biphenyl-4'-yl 4-(hexa-1,5-dien-3-yloxycarbonyldecyloxy)benzoate



Compound **7.7** (435 g mol^{-1})	2.00 g, 4.60 mmol
Compound **2.2** (345 g mol^{-1})	1.59 g, 4.60 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 3.00 g, 93 %.

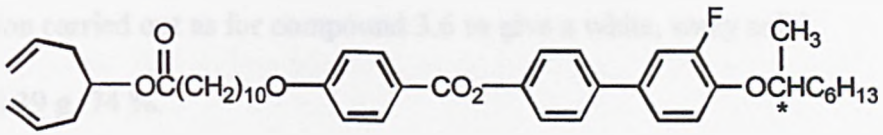
IR ν_{max}(cm^{-1}): 1070, 1170, 1270, 1500, 1610, 1730, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.2-1.5 m [27H], 1.56 m [1H], 1.73 m [1H], 2.3 t [2H], 2.4 t [2H], 4.0 t [2H], 4.3m [1H], 5.13 m [4H], 5.32 m [1H], 5.75 m [2H], δ6.9 d [2H], δ7.0 t [1H], δ7.30 m [4H], δ7.6 d [2H], 8.2 d [2H].

OR: $[\alpha]_D = +1.96°$.

Compound **7.11**

(*R*)-3-Fluoro-4-(1-methylheptyloxy)biphenyl-4'-yl 4-(hepta-1,6-dien-3-yloxycarbonyldecyloxy)benzoate



Compound **7.7** (435 g mol^{-1})	2.00 g, 4.60 mmol
Compound **2.3** (359 g mol^{-1})	1.65 g, 4.60 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 2.79 g, 85 %.

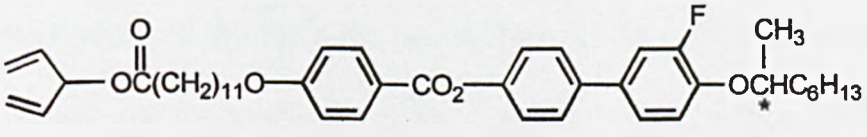
IR ν_{max}(cm^{-1}): 1070, 1170, 1270, 1500, 1610, 1730, 2860, 2940.

^{1}H NMR: δ 0.9 t [3H], 1.2-1.5 m [27H], 1.56 m [1H], 1.73 m [1H], 2.3 t [2H], 2.4 t [4H], 4.0 t [2H], 4.3m [1H], 5.0 quint [1H], 5.1 m [4H], 5.75 m [2H], 6.9 d [2H], 7.0 t [1H], 7.30 m [4H], 7.6 d [2H], 8.2 d [2H].

OR: $[\alpha]_D$ = +2.21°.

Compound **7.12**

(*R*)-3-Fluoro-4-(1-methylheptyloxy)biphenyl-4'-yl 4-(penta-1,4-dien-3-yloxycarbonylundecyloxy)benzoate



Compound **7.7** (435 g mol^{-1})	2.00 g, 4.60 mmol

Compound **5.3** (345 g mol^{-1})	1.59 g, 4.60 mmol
Potassium carbonate	5 g
Butanone (dry)	100 ml

Preparation carried out as for compound **3.6** to give a white, waxy solid.

Yield = 2.39 g, 74 %.

IR $\nu_{max}(cm^{-1})$: 1070, 1170, 1270, 1500, 1610, 1730, 2860, 2940.

^1H NMR: δ 0.9 t [3H], 1.2-1.5 m [29H], 1.56 m [1H], 1.73 m [1H], 2.3 t [2H], 4.0 t [2H], 4.3m [1H], 5.30 m [4H], 5.7 t [1H], 5.8 m [2H], 6.9 d [2H], 7.0 t [1H], 7.30 m [4H], 7.6 d [2H], 8.2 d [2H].

OR: $[\alpha]_D = +2.34°$.

2.4.8 Method For Polymerisation of Monomers

After the initial studies were completed (see **3.1**) using monomers derived from schemes **1** and **2** it was decided to carry out all subsequent polymerisations using a standard method. This will be described using monomer **3.9** as an example [3].

Monomer **3.9** (0.75 g, 1.41 mmol) and Irgacure 184 photocuring agent (14.4 mg, 0.071 mmol, 5 mol%) were dissolved in dry DCM (5 ml). The resulting solution was spread evenly onto a sheet of boro-silicate glass (180 × 250 mm) which was dried (80 °C). When dry, a second sheet of pre-heated (80 °C) boro-silicate glass was placed over the first and pressed down firmly, spreading the molten monomer into a thin film. The resulting 'sandwich' was placed under a Philips UVA sun-lamp and irradiated for 2h.

The glass plates were then separated and the polymer was washed off with dry DCM, which was removed *in vacuo*. The polymer sample was then purified by dissolving it in dry DCM (10 ml), putting equal quantities of the resulting solution into four 25 ml centrifuge tubes and precipitating the polymer by the addition of sufficient methanol (up to 25 ml). The tubes were spun in a centrifuge (11,000 rpm, 10 min) then the methanol layer was decanted off, leaving the polymer in the bottom of the tubes. This process was repeated until all the unreacted monomer was removed (single spot TLC, usually requires three precipitations) and the polymer was dissolved in DCM (10 ml) This solution was passed through a membrane filter (0.5 μm). The solvent was removed *in vacuo* and the resulting purified polymer **3.9** was then dried (80 °C).

Yield = 0.47g, 63%.

All polymerisations of monomers from scheme **4** onwards were carried out using 5 wt% of initiator as this gives improved yield but has little effect on molecular weight (see later).

2.4.9 References

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2 G. M. Anantharamaiah and K. M. Sivanadaiah (1977) *J. Chem. Soc., Perkin Trans. 1*, 490; S. Hanessian, T. J. Liak and B. Vanasse (1981) *Synthesis*, 396.

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3.1 Optimisation Of Polymerisation Procedure

Preliminary experiments were carried out to optimise the conditions for polymerisation of monomers. Monomers from schemes **1** and **2** were used, which were synthesised specifically for this purpose. Although they were not expected to give the required SmC* phases, they were relatively inexpensive and simple to synthesise. Two experiments were carried out on the different monomer systems to see what difference they made to the molecular weight distribution of the resulting polymers. Firstly, the effect of length of time that the reaction mixture was subject to irradiation with UV light was investigated and secondly, the effect of altering the concentration of the photo-initiator. Benzil was used as the initiator in these first experiments.

Once these initial experiments had been carried out and the basic conditions for the polymerisation reaction had been determined, a comparison of benzil and Irgacure 184 (Ciba-Giegy), a specialist photocuring agent, was conducted. The monomers used for these experiments were synthesised from scheme **3**, and it was hoped that these polymers would display the SmC* phase.

3.1.1 Results of varying length of reaction time.

All polymerisations carried out using 2.5 mol% benzil as initiator.

Table **3.1.1** Monomer **2.4**

Time/min	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
10	6,550	8,320	1.27	14.7
30	7,000	9,240	1.32	15.7
60	7,680	10,700	1.39	17.3
120	8,340	11,900	1.43	18.8

Table **3.1.2** Monomer **2.5**

Time/min	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
10	5,930	7,000	1.18	12.9
30	6,730	8,080	1.20	14.7
60	6,95	8,410	1.21	15.2
120	7,520	9,400	1.25	16.4

Table **3.1.3** Monomer **2.6**

Time/min	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
10	5,110	5,720	1.12	10.8
30	5,140	5,860	1.14	10.9
60	5,390	6,140	1.14	11.4
120	5,440	6,420	1.18	11.4

Table **3.1.4** Monomer **1.2**

Time/min	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
10	10,100	14,300	1.42	12.1
30	12,100	20,400	1.69	14.5
60	13,500	27,400	2.03	16.1
120	21,300	60,700	2.85	25.4

As can be seen from tables **3.1.1** to **3.1.3**, the mono-substituted dienes all behave in a similar way. The length of time allowed for reaction has little effect on the molecular weight distribution, as would be expected for chain growth polymerisation. This is because the lifetime of a propagating radical will be very small in relation to the length of the experiment. The small increase in molecular weight that is seen could be due to the physical nature of the bulk reaction mixture changing over the course of time and having an effect on the relative rates of propagation and termination.

The results for the polymerisation of monomer **1.2**, shown in table **3.1.4**, show clearly that the length of reaction time has a very large effect on the molecular weight distribution of the resultant polymer. There is a doubling in DP and PDI when increasing reaction time from ten minutes to two hours. One possible explanation for this result is the presence of different isomers in the starting material, which may have an effect upon the relative rates of propagation and termination. This explanation is discussed in more detail later. Due to the fact that the molecular weight distribution for polymers synthesised from monomer **1.2** show a large dependence on reaction time and also because these results were somewhat unreproduceable (one polymer of monomer **1.2** had a PDI of eight), no more monomers were synthesised from 1,5-hexadiene-3,4-diol.

3.1.2 Results of varying the concentration of initiator.

Table **3.1.5** Monomer **2.4**

mol%	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
5	7,340	10,600	1.45	16.7
10	6,130	9,010	1.47	13.9

Table **3.1.6** Monomer **2.5**

mol%	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
1	5,480	6,630	1.21	12.1
5	5,530	6,580	1.19	12.2

Table **3.1.7** Monomer **2.6**

mol%	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
1	5,680	6,130	1.08	11.9
5	5,180	5,750	1.11	10.9

Shown in tables **3.1.5** to **3.1.7** are the results of the experiments to determine what effect the concentration of the photoinitiator had upon the molecular weight distribution. The reaction time was 1 hour and the photoinitiator used was benzil. Polymerisations of monomers **2.5** and **2.6** were carried out with 1 and 5 mol% initiator, whereas polymerisations of monomer **2.4** were carried out with 5 and 10 mol% initiator. The reason for the increased initiator concentrations was that, using similar conditions to the other two monomers **2.5** and **2.6**, negligible product was obtained with monomer **2.4**.

What these results show is quite surprising, in that the initiator concentration at the start of the reaction has very little effect upon molecular weight. This is unusual, as the molecular weight is inversely proportional to the square root of the initiator concentration. This would mean that if the initiator concentration was doubled, then the molecular weight of the resultant polymer would be smaller by a factor of $\sqrt{2}$, which is approximately equal to 1.4 (see references **1.4.8**). Looking at the results in table **3.1.5**, were the initiator concentration of one experiment is double that of the other, the molecular weight is not 1.4 times smaller. Looking at tables **3.1.6** and **3.1.7**, where the difference in initiator concentration is a factor of five, there is even less difference between the molecular weights for the different concentrations of initiator than there was in table **3.1.5**.

Whilst the concentration of initiator has little effect on molecular weight, it does have an effect on the yield of polymer from the reaction. Increasing the concentration of initiator always increased the yield of polymer obtained.

3.1.3 Which Initiator ?

The following tables contain the details of the initial quantity (I.Q.) of monomer used in the polymerisation reaction, the resulting yield of polymer produced after workup (table **3.1.8**) and the GPC data of the polymers (table **3.1.9**). The tables contain data on polymers produced from monomers synthesised from scheme **3**.

Table **3.1.8**

Polymer	I.Q./g	Yield/g	Yield/%
3.9b	0.50	0.15	30
3.9i	0.75	0.47	63
3.10b	0.50	0.08	16
3.10i	0.50	0.15	30
3.11b	0.50	0.05	10
3.11i	0.50	0.13	26

Table **3.1.9**

Polymer	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
3.9b	7,300	9,730	1.33	13.7
3.9i	8,210	12,400	1.51	15.4
3.10b	6,080	7,460	1.23	11.1
3.10i	7,120	9,550	1.34	13.0
3.11b	4,720	5,470	1.16	8.40
3.11i	5,180	6,200	1.20	9.17

Tables **3.1.8** and **3.1.9** contain the results obtained by polymerising monomers derived from scheme **3**. The object of these experiments was to determine if initiation with Irgacure 184 (suffix **i**) produced significantly different results to initiation with benzil (suffix **b**). It can be seen from table **3.1.9** that there is no large difference between the molecular weights of the polymers using the different initiators, except that using Irgacure 184 results in slightly higher molecular weight and PDI value for the polymer. However, table **3.1.8** shows that initiation by Irgacure 184 gives approximately twice the yield of polymer. For this reason all subsequent polymerisations were carried out using Irgacure 184 as photoinitiator.

The results from this study enabled a standard procedure for polymerisation of the monomers to be made, and this is described in the experimental section.

3.2 Results of Polymerisations

3.2.1 Quantities and Yields of Polymerisations

The following tables contain the details of the initial quantity (I.Q.) of monomer used in the polymerisation reaction and the resulting yield of polymer produced, after workup. Each table contains polymers produced from monomers synthesised from series **3** to **7**, using the standard procedure for polymerisation as described in the experimental section.

Table **3.2.1** Scheme **3**

Polymer	I.Q./g	Yield/g	Yield/%
3.6	1.50	1.34	89
3.7	2.00	0.95	48
3.8	1.50	0.52	35

Table **3.2.2** Scheme **4**

Polymer	I.Q./g	Yield/g	Yield/%
4.19	1.00	0.80	80
4.20	1.00	0.17	17
4.21	1.00	0.31	31
4.22	1.00	0.60	60
4.23	1.00	0.44	44
4.24	1.10	0.28	25

Table **3.2.3** Scheme **5**

Polymer	I.Q./g	Yield/g	Yield/%
5.4	1.00	0.70	70
5.5	1.00	0.83	83
5.6	1.00	0.32	32
5.7	1.88	1.48	79
5.8	1.57	0.98	62
5.9	1.70	1.17	69
5.10	1.00	0.90	90

Table **3.2.4** Scheme **6**

Polymer	I.Q./g	Yield/g	Yield/%
6.4	1.00	0.94	94
6.5	0.75	0.28	37
6.6	1.00	0.73	73
6.7	1.00	0.54	54
6.8	1.00	0.45	45
6.9	1.00	0.63	63

Table **3.2.5** Scheme **7**

Polymer	I.Q./g	Yield/g	Yield/%
7.8	2.00	1.45	73
7.9	2.00	1.73	87
7.10	2.00	1.57	79
7.11	2.00	1.13	57
7.12	2.00	1.87	94

It will be noticed that a pattern has developed in the yield of polymerisations. This is that almost without exception, for a given side chain, the pentadienes are higher yielding than the hexadienes, which are higher yielding than the heptadienes. As an example, consider the three polymers, **4.22**, **4.23** and **4.24** from table **3.2.2**. The monomers all have the same side chain. It is noticed that the yield decreases in the order **4.22** to **4.23** to **4.24**. This trend, which is also shown by most of the other

series of polymerisations, is discussed later in the section on termination of polymerisation.

3.2.2 Molecular Weight Distributions

The following tables contain the details of the molecular weight data, obtained by GPC, of the polymers produced from monomers synthesised from series **3** to **7**.

Table **3.2.6** Scheme **3**

Polymers	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
3.6	10,300	23,700	2.30	21.0
3.7	6,840	10,200	1.49	13.5
3.8	3,880	4,750	1.22	7.46

Table **3.2.7** Scheme **4**

Polymers	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
4.19	10,500	21,500	2.12	19.7
4.20	7,230	9.860	1.36	13.2
4.21	5,860	7,160	1.22	10.5
4.22	8,300	11,700	1.41	14.5
4.23	7,440	9,810	1.32	12.7
4.24	4,660	5,790	1.19	7.74

Table **3.2.8** Scheme **5**

Polymers	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
5.4	8,710	15,300	1.76	13.9
5.5	4,490	6300	1.40	7.00
5.6	3,610	4,410	1.22	5.51
5.7	9,250	18,200	1.97	13.8
5.8	7,620	12,100	1.58	11.1
5.9	4,340	5,720	1.32	6.22
5.10	5,220	7,390	1.42	7.63

Table **3.2.9** Scheme **6**

Polymers	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
6.4	11,900	24,000	2.02	17.0
6.5	5,710	7,030	1.23	7.87
6.6	10,900	20,300	1.87	14.7
6.7	9,500	23,300	2.45	12.6
6.8	6,140	8,470	1.38	8.02
6.9	9,330	19,200	2.06	12.4

Table **3.2.10** Scheme **7**

Polymers	$\overline{M}_n$	$\overline{M}_w$	PDI	DP
7.8	7,890	13,300	1.69	12.3
7.9	12,800	41,400	3.22	18.7
7.10	5,320	11,600	2.18	7.61
7.11	4,520	6,160	1.36	6.34
7.12	13,400	44,800	3.34	19.1

There are a number of trends which are present throughout the data in the above tables and also the data in tables in the previous section regarding the molecular weight of polymers synthesised from schemes **2** and **3**.

The most obvious trend is that the DP of polymers with the same side chain decreases in the order; polypentadiene (7.63 to 19.7) > polyhexadiene (7.00 to 16.4) > polyheptadiene (5.51 to 11.9). This occurs without exception for all the series of polymers. Another observation is that the DP is quite low for all the polymers (5.51 to 19.7), especially the poly-heptadienes (5.51 to 11.9). The conclusions drawn from these observations will be discussed later in the section on termination of polymerisation.

The PDI for the polymers is low, most have values below two. This is probably not surprising as the DP for most of the polymers is low as well. The only exceptions to this, with PDI values over 3, are the polypentadienes, polymers **7.9** and **7.12**. The probable reason for this is that the polymerisations for these compounds proceeded to a high conversion of monomer, giving yields of approximately 90%. It has been shown, that free radical chain growth polymerisations carried out to a high conversion can lead to high values of PDI [1].

3.2.3 Reference

1 G. Odian (1991) *Principles of Polymerisation*, Wiley Interscience, New York, p. 296.

3.3 Thermal Transitions of Monomers

The following tables show the thermal transitions of the polymers synthesised from series **1** to **7**, as determined by DSC (heating / cooling rate 10 °C/min). Phase transitions are quoted as the onset of the transition. Phase identification was carried out by optical microscopy. All temperatures quoted are in degrees centigrade (°C).

Table **3.3.1** Scheme **1**

Monomer 1.2	Tg	C-SmA	SmA-Iso	C-Iso
1st heat	-	-	-	91.8
cool	-12.3	-	57.6	-
2nd heat	-16.2	24.4	69.4	-

Table **3.3.2** Scheme **2**

Monomer		C-SmA	SmA-Iso	C-Iso
2.4	heat	-	-	55.1
2.4	cool	23.6	31.6	-
2.5	heat	25.0	29.6	-
2.6	heat	-	-	31.4
2.6	cool	6.3	27.0	-

Table **3.3.3** Scheme **3**

Monomer	C-SmA	SmA-Iso	C-Iso
3.6	20.3	26.4	-
3.7	-	-	-14.9
3.8	-	-	0.6
3.9	-	-	22.6
3.10	-	-	23.7
3.11	-	-	25.2

Table **3.3.4** Scheme **4**

Monomer	C-Iso
4.19	7.1
4.20	7.6
4.21	7.3
4.22	17.7
4.23	20.3
4.24	24.0

Table **3.3.5** Scheme **5**

Monomer	C-SmC*	SmC*-SmA	SmA-N*	N*-Iso	SmA-Iso
5.4	59.7	84.3	-	-	109.2
5.5	52.6	86.1	108.0	110.2	-
5.6	64.2	80.6	99.6	102.8	-
5.7	39.5	88.6	-	-	111.6
5.8	32.5	68.0	-	-	92.9
5.9	38.5	84.1	-	-	100.8
5.10	58.2	85.7	-	-	111.5

Table **3.3.6** Scheme **6**

Monomer	C-Iso
6.4	28.7
6.5	12.8
6.6	38.5
6.7	36.7
6.8	36.8
6.9	45.5

Table **3.3.7** Scheme **7**

Monomer	C-SmC*	SmC*-SmA	SmC*-Iso	SmA-Iso
7.8	24.9	52.1	-	57.2
7.9	51.4	56.7	-	58.0
7.10	41.2	-	50.7	-
7.11	35.2	46.1	-	50.0
7.12	34.5	-	59.2	-

Possibly the most unusual results were produced by monomer **1.2**, as shown in table **3.3.1**. On the first heat the compound melts from the crystal to the isotropic liquid at 91.8 °C. However, on the subsequent cool cycle, a SmA phase is observed at 57.6 °C, which then becomes a glass, with a Tg at -12.3 °C. On the next heat cycle there is transition from the glass to a crystal phase with a Tg at 16.2 °C, which then goes on to melt at 24.4 °C into the SmA phase. The transition to the isotropic liquid occurs at 69.4 °C. The second heat and cool cycle is repeatable, as shown in figure **5.7**. After allowing the sample to stand at room temperature overnight, the compound crystallises and its behaviour reverts to that as shown by the first heat.

There are two possible reasons to account for this unusual behaviour, which is not exhibited by any of the other monomers from this work. Firstly, the lowering of the melting point and the appearance of a mesophase is probably due to the fact that monomer **1.2** is a mixture of isomers (see later) and under the fairly rapid cooling of the DSC experiment, this could lead to difficulty in molecular packing and a failure to crystallise. However, if left overnight, crystallisation clearly takes place. Secondly, there is an appearance of a Tg. This is not usual for a monomer but probably comes about because the extended molecule is long, due to the presence of the two side chains. However, this apparent Tg may simply be due to release of stress energy, caused by the fairly rapid cooling rate.

Of the monomers shown in table **3.3.2**, the pentadiene, monomer **2.4** and the heptadiene, monomer **2.6**, both give a monotropic SmA phase, the hexadiene, monomer **2.5** does not give any mesophases. The SmA phases occurs at a higher

temperature in the pentadiene **2.4** than the heptadiene **2.6**. This appears to be common to all series of monomers and will be discussed later in this section.

All the other monomers with side chains containing two phenyl rings, i.e. monomers from series **3** and **4**, with the exception of monomer **3.6**, show no liquid crystalline material. Monomer **3.6** displays a narrow (6.1 °C) SmA phase.

The remaining monomers all contain 3 phenyl rings in the side chain. Of these, monomers from series **5**, show the highest phase stability. All the compounds display mesogenic behaviour up to at least 90 °C. All the compounds also display a SmC* to SmA transition. Monomers **5.5** and **5.6**, also display a narrow N* phase.

None of the monomers from series **6** exhibit a mesophase. As the structure of these compounds is similar to that of the monomers from series **5**, it would seem that the substitution of the 2-methylbutyl group with the 1-methylheptyl group greatly reduces the stability of the mesophase, to such an extent that monomers **6.4** to **6.9** do not display liquid crystalline behaviour.

All compounds from series **7** exhibit a SmC* phase, with monomers **7.8**, **7.9** and **7.11** also exhibiting a SmA phase. The isotropisation temperatures of these compounds are much lower than those of monomers from series **5**, probably because of the lower phase stability produced by the inclusion of the 1-methylheptyl group and the lateral fluoro-substituent.

There are two trends that are displayed by the monomers that display liquid crystalline behaviour. The first is that, for a given side chain and diene, the phase stability increases with increasing length of the spacer. For example, from series **7**, the monomers **7.8, 7.9** and **7.11** are all pentadienes with spacer lengths of 7, 10 and 11 methylene units and isotropisation temperatures of 57.2 °C, 58.0 °C and 59.2 °C respectively.

The second is that, for a given side chain and spacer group, the isotropisation temperature increases in the order; hexadiene < heptadiene < pentadiene. For example, monomers **5.8** (hexadiene), **5.9** (heptadiene) and **5.7** (pentadiene) all have the same mesogen, a spacer 10 methylene units long, and have isotropisation temperatures of 92.9 °C, 100.8 °C and 111.6 °C respectively. This is probably due to the diene group disrupting the formation of the mesophase.

The pentadiene is not only symmetrical about the point of attachment of the side chain to the diene moiety, but is also the smallest of the three diene moieties, so therefore its presence will have the least detrimental effect on the formation of mesophases. The heptadiene is also symmetrical about the point of attachment, but it is the largest of the three diene moieties so its size will adversely affect the formation of mesophases. The hexadiene is not symmetrical about the point of attachment, and so this, together with the size of the diene moiety appears to severely disrupt the formation of mesophases.

3.4 Thermal Transitions Of Polymers

The following tables show the thermal transition tempeatures and mesophase morphology of the polymers synthesised from series **1** to **7**, as determined by DSC (heating / cooling rate 10 °C/min) and optical microscopy. All temperatures quoted are in °C. The clearing point is quoted as the mid point of the transition. The thermal data for polymers from series **1** which are shown in table **3.4.1** are from table **3.1.4**, the suffix denoting the duration of irradiation with UV radiation. The thermal data for polymers from series **2** which are shown in table **3.4.2** are from tables **3.1.5**, **3.1.6**, and **3.1.7** using 5 mol% initiator.

Table **3.4.1** Series **1**

Polymer	g-SmA	SmA-Iso	SmA-Iso #2
1.2-10min	6.7	106.0	-
1.2-60min	20.5	137.6	-
1.2-120min	19.1	134.3	147.1

Table **3.4.2** Series **2**

Polymer	g-SmA	SmA-Iso
2.4	19.6	76.0
2.5	23.3	55.8
2.6	22.6	70.7

Table **3.4.3** Series **3**

Polymer	g-SmA	SmA-Iso
3.6	23.3	65.0
3.7	24.2	39.5
3.8	14.0	22.6
3.9i	2.8	30.8
3.10i	2.3	26.9
3.11i	4.4	44.2

Table **3.4.4** Series **4**

Polymer	g-SmA	SmA-Iso
4.19	13.4	32.0
4.20	4.6	19.7
4.21	-10.4	14.8
4.22	-1.8	52.6
4.23	11.1	34.1
4.24	7.7	27.7

Table **3.4.5** Series **5**

Polymer	g-SmC*	SmC*-Iso
5.4	30.3	171.2
5.5	28.9	110.9
5.6	18.8	108.2
5.7	19.0	171.7
5.8	22.6	153.7
5.9	13.8	127.3
5.10	14.0	141.0

Table **3.4.6** Series **6**

Polymer	g-SmC*	SmC*-Iso	g-Iso
6.4	-	-	24.3
6.5	-	-	11.3
6.6	19.7	124.4	
6.7	20.2	125.4	
6.8	13.1	112.3	
6.9	15.7	129.3	

Table **3.4.7** Series **7**

Polymer	g-SmC*	SmC*-Iso
7.8	14.9	74.4
7.9	14.1	116.1
7.10	5.7	74.4
7.11	5.2	61.8
7.12	10.9	108.6

It will be seen from the above tables that the main effect of polymerisation is either the appearance of a liquid crystal phase, or the increase in thermal stability of the liquid crystal phase over those exhibited by the monomers.

Polymers from series **1** and **2** give a SmA phase as expected, as all the monomers from these series exhibit a SmA phase. The range of the SmA phase ranges from 32.5 °C for polymer **2.5**, to 128 °C for polymer **1.2-60min**. This large difference in ranges, as polymers **1.2-60min** and **2.5** are both polyhexadienes, is due to the fact that polymer **1.2** has a higher DP and also has two side chains per repeat unit as opposed to polymer **2.5** which has one.

Polymers from series **3** all exhibit a SmA phase, whilst only monomer **3.6** exhibits a liquid crystal phase, in this case a SmA phase. The range of the SmA phase ranges from 8.6 °C for polymer **3.8** to 41.7 °C for polymer **3.6**.

Polymers from series **4** all exhibit a SmA phase, whilst none of the monomers exhibit a liquid crystal phase. The range of the SmA phase ranges from 15.1 °C for polymer **4.20** to 54.4 °C for polymer **4.22**.

Polymers from series **5** all exhibit a SmC* phase. This was to be expected as all the monomers from series **5** exhibit a SmC* phase. However, the SmA phase exhibited by all the monomers and the N* phase exhibited by polymers **5.5** and **5.6** (see figure **5.9**) are all absent from the polymers (see figure **5.10**). The range of the SmC* phase ranges from 82.0 °C for polymer **5.5** to 152.7 °C for polymer **5.7**.

Polymers **6.4** and **6.5** do not show a mesophase, suggesting that with this side chain a spacer length of 7 methylene units is too short to allow sufficient decoupling between the mesogen and the polymer backbone. Those polymers from series **6** with a liquid crystal phase exhibit the SmC* phase. None of the monomers from this series exhibits a liquid crystal phase, so it would seem that with a spacer of sufficient length stabilisation of the SmC* phase occurs. The range of the SmC* phase ranges from 99.2 °C for polymer **6.8** to 113.6 °C for polymer **6.9**.

Polymers from series 7 all exhibit the SmC* phase, as do all the monomers in this series. However, as happens in series **5**, the SmA phase exhibited by monomers **7.8**, **7.9** and **7.11** is lost in the polymers. The range of the SmC* phase ranges from 56.6 °C for polymer **7.11** to 102.0 °C for polymer **7.9**.

Results from series **1** were taken from the polymers which had been polymerised for different lengths of time to show what effect the molecular weight variation has on the thermal transitions, as shown in table **3.4.1**. All three polymers exhibit a SmA phase. Polymer **1.2-10min** shows a Tg at 6.7 °C and an isotropisation temperature of 106 °C. If this is compared with polymer **1.2-60min**, with an increase in DP from 12.1 to 16.1, there is a corresponding increase in the Tg, to 20.5 °C, and the isotropisation temperature, to 137.6 °C. This is significant, as it clearly shows that at these relatively low DP values, there is an increase in the entanglement of the backbones, hence the higher Tg, and also the temperature range of the mesophase.

The main difference between these polymers and polymer **1.2-120min** is that polymer **1.2-120min** behaves as a mixture of two polymers, one low molecular weight and the other higher molecular weight. This is observed in both the molecular weight data and the thermal analysis data. The DP has increased to 25.4 and the PDI has increased to 2.85. The molecular weight, as determined by GPC shows a bimodal distribution. This has little effect on the Tg, suggesting that the relationship between molecular weight and Tg does not increase any further after the incorporation of 16 repeat units. However, there is a marked difference in clearing temperature. There are two clearing points observed, both by optical microscopy and by DSC. The first of these, at 134.3 °C, corresponds to the clearing point of the low molecular weight fraction, and appears to be similar to that of polymer **1.2-60min**. The second clearing point, of 147.1 °C corresponds to the higher molecular weight fraction. This clearly shows that the isotropisation point continues to increase with increasing molecular weight. There is evidence from the literature to suggest that these observations are correct, that is, there is a significant increase in Tg up to a DP of approximately 10, and that there is a significant increase in isotropisation temperature up to a DP of approximately 100 [1].

All the other series of polymers can be split into two groups, those with two ring mesogens (series **2**,**3** and **4**) and those with three ring mesogens (series **5**,**6** and **7**). All the two ring systems, without exception, exhibit a SmA phase, this despite series **3** and **4** possessing mesogens which were expected to give polymers exhibiting a SmC* phase. The requirement for the presence of a SmC* phase appears to be a three ring mesogen, as all such polymers, if they display a mesophase, exhibit a SmC* phase.

They may also exhibit a narrow range SmA phase below the clearing point, but the transition is of too low an energy to be detected by DSC, and the optical texture is poor, so assignation by optical microscopy is difficult.

As expected, the clearing points of the polymers with three ring mesogens are higher than those of the polymers with two ring mesogens. For the group with two ring mesogens the clearing points of polymers in series **2** are higher than those of polymers from series **3** and **4**, for the same polymer backbone. The clearing points of polymers within series **3** and **4**, are similar for polymers with the same spacer length and backbone. This is probably because the monomers from series **2** are more mesogenic than the monomers for series **3** and **4**, none of which exhibit a mesophase, apart from monomer **3.6**, which exhibits a SmA phase.

The pattern for the group of polymers with three ring mesogens is that the clearing point decreases in the order, series **5**, **6** and **7**. This pattern is due to the structure of the mesogens. The mesogen from series **5** would be expected to give the highest isotropisation temperature, as the 2-methylbutyl group increases the stability of a SmC* phase over that produced by the 1-methylheptyl group in the mesogen of polymers from series **6** [2]. The polymers in series **7** have a lateral fluoro-substituent and the use of an ether link to the chiral group instead of an ester, in the mesogenic group. This results in a lower clearing point.

For a given diene and mesogen, the clearing point increases with increasing spacer length from 7 to 10 carbon atoms. The polymers with 11 carbon atom spacers have

similar clearing points to those polymers with spacers 10 carbon atoms long. For example, the polypentadienes from series **7** have clearing points of 74.4, 116.1 and 108.6 °C and spacer lengths of 7, 10 and 11 carbon atoms respectively. This supports the theory that a flexible spacer decouples the anisotropic mesogen from the isotropic polymer backbone, allowing it to form a more stable mesophase. It would be expected that the flexibility of the spacer will increase with length. This is observed with polymers from series **6**. The polymers **6.4** and **6.5**, with a spacer length of 7 atoms, show no mesophase. The other polymers in this series have spacers 10 or 11 atoms long, and all exhibit a wide SmC* phase.

Within each series of polymers, for a given spacer length, the clearing points decrease in the order polypentadiene, polyhexadiene and polyheptadiene. However, this does not appear to be because the ability of the polymer to stabilise the mesophase decreases in that order, this order is more likely to come about because of the differing DP of each polymer system. Within series **2** and polymers **3.9i**, **3.10i** and **3.11i** from series **3**, where the different polymer systems all have comparable values of DP, there is a different order of phase stability. The clearing points reduce in the order polypentadiene > polyheptadiene > polyhexadiene. This is probably because, once the DP effect is removed, the flexibility of the backbone will show a real effect on the clearing point. Both the polypentadiene and the polyheptadiene have a flexible dimethylene linking group between the rings in the polymer backbone, whereas, the polyhexadiene has a much less flexible methylene linking group. It would be expected that the polyheptadiene would be the most flexible backbone of the three, so if a high

enough DP was obtained for all three systems, then the clearing point could decrease in the order polyheptadiene > polypentadiene > polyhexadiene.

The Tg values for most of the polymers are at or near room temperature, regardless of the polymer structure or series. It would seem that the DP of the polymers is large enough such that variations of Tg for different values of DP are small or not observed. The only polymers which show markedly lower values of Tg, being at or near 0 °C, are those from series **3** and **4**, apart from polymers **3.6** and **3.7**, where the clearing point of the SmA phase is near the Tg. It would seem that the low isotropisation temperature, at a temperature near to the Tg, lowers the temperature at which the polymer is stable as a glass.

3.4.1 References

1 V. Percec and C. Pugh, (1989) *Molecular Engineering of Predominantly hydrocarbon-based LCPs* in McArdle, C. B., Ed., *Side Chain Liquid Crystal Polymers*, p. 53-57.

2 T. E. Mann (1996) PhD Thesis, University of Hull.

3.5 Comparison with other Systems

The thermal transitions of some of the polymers in this study will be compared to examples of different polymer systems but incorporating the same mesogenic groups, some of which were synthesised at Hull (the Baylis-Hillman type) [1] and some elsewhere [2]. Two of the polymer series will be discussed, those from series **2** and those from series **7**. All temperatures in tables are in °C.

3.5.1 Polymers from Series 2

Comparison of the thermal properties between polymers from series **2** and other polymer systems incorporating the mesogenic group as shown in figure **3.5.1** are shown in table **3.5.1** [1,2]. All the polymers have a spacer of similar length.

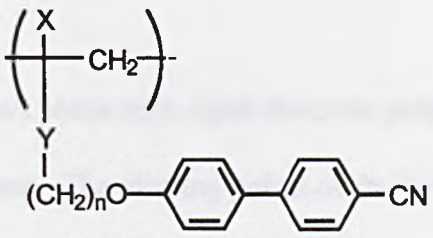


Figure **3.5.1**

Table **3.5.1**

X	Y	n	g	SmC	SmA	Iso
H	CO_2	11	25	30	145	
CH_3	CO_2	11	-	40	121	
CN	CHOH	10	-	25	99	
$COCH_3$	CHOH	10	-	38	66	
CO_2CH_3	CHOH	10	-	30	49	

The DP and PDI values for the Baylis-Hillman type polymers (Y = CHOH; DP ≈ 6, DPI = 1.2 to 1.5) are similar to those for polymers from series **2**, so direct comparison between these systems can be made. The thermal data for the polyacrylate (X = H) and polymethacrylate (X = CH_3) were not accompanied by any molecular weight data, so a direct comparison may not be valid, but will probably give a reasonable indication of any differences in thermal properties between the two different polymer systems.

As can be seen from table **3.4.2**, the Tg of polymers from series **2** occurs between 19 and 23 °C, which is lower than the Tg of any of the polymers in table **3.5.2**. This is to be expected as, apart from the polyacrylate, the polymers have bulky or polar groups on the polymer backbone. In fact, the Tg for the polyacrylate, which occurs at 25 °C, is close to those of polymers from series **2**, probably because none of these polymers possess bulky groups on the polymer backbone.

All the polymers give a SmA phase only, apart from the polyacrylate, which also exhibits a narrow SmC phase. The clearing points of the Baylis-Hillman type polymers are similar to those of polymers from series **2**. This is probably to be expected, as these polymers all have small values of DP. This can be contrasted with the polyacrylate and polymethacrylate, whose clearing points are 145 and 121 °C respectively. This is probably due to these two polymers having high values of DP, as acrylates and methacrylates polymerise easily to high molecular weights. This increase in DP will stabilise the mesophase.

3.5.2 Polymers from series 7

Comparison of the thermal properties between polymers from series 7 with other polymer systems incorporating the same mesogenic group as shown in figure **3.5.2** are given in table **3.5.2** [3]. All the polymers have a spacer of similar length.

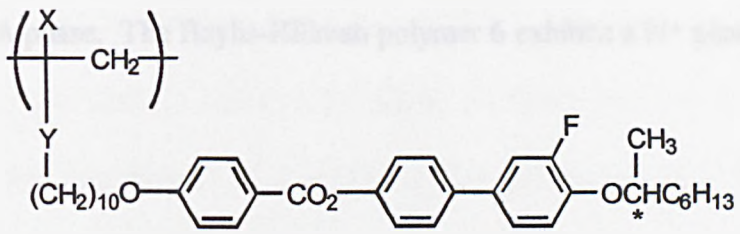


Figure **3.5.2**

Table **3.5.2**

	X	Y	g	Sm	SmC*	SmA	N*	Iso
1	H	CO_2	31		49	126	-	137
2	H	CO_2CH_2	28		53	134	-	147
3	CH_3	CO_2CH_2	65		65	120	-	144
4	Cl	CO_2CH_2	51		52	130	-	142
5	CN	CHOH	-		74	-	-	135
6	$COCH_3$	CHOH	-		2.5	-	59	69
7	CO_2CH_3	CHOH	-		18	-	-	90

Direct comparisons between polymers from series 7 and those in table **3.5.2** can be made since the DP values are comparable. Polymers **1** to **4** have DP values in the range 12-15, and polymers **5** to **7** have DP values in the range 8-10.

All the polymers in table **3.5.2** exhibit a wide range SmC* phase, as do those from series 7. It is clear that, regardless of the structure of the polymer backbone, this mesogenic side chain strongly favours the formation of the SmC* phase. It will be

seen from table **3.5.2** that all the polyacrylate type derivatives (polymers **1** to **4**) have a higher Tg temperature relative to the other polymers, presumably due to the rigidity of the polymer backbone. The only exception to this is the Baylis-Hillman type polymer **5**, which has a Tg at 74 °C. All the polyacrylate type polymers **1** to **4** possess a SmC* phase that is stable to above 120 °C, and also a SmA phase in the range 137 to 147 °C. None of the Baylis-Hillman type polymers **5** to **7** or polymers from series **7** exhibit a SmA phase. The Baylis-Hillman polymer **6** exhibits a N* phase from 59 to 69 °C.

Polymers **1** to **4** also show one or more higher order smectic phases, which are shown in the table **3.5.2** as Sm are not described in detail. The greater mesophase stability afforded by these polymer backbones probably allows the appearance of these phases.

The polymers from series **7** have Tg values similar to those of polymers **6** and **7**, occurring below room temperature, and all possess a room temperature SmC* phase. However, polymers **7.9** and **7.12**, both polypentadienes with spacer lengths 10 and 11 methylene units respectively, exhibit a SmC* phase from below room temperature to over 100 °C. This gives these polymers a very wide SmC* phase, 102 °C for polymer **7.9** and 97.7 °C for polymer **7.12**. These polymers have a much wider SmC* phase than any of the polymers in table **3.5.2**. The polypentadiene backbone, with a spacer of sufficient length, stabilises a wide range SmC* phase, whilst hindering the formation of higher order smectic phases.

3.5.3 References

1 A. W. Hall, D. Lacey J. S. Hill and D. G. McDonnell (1994) *Supramol. Sci.*, **1**, 21.

2 V. Percec and C. Pugh (1989) *Molecular Engineering of Predominantly hydrocarbon-based LCPs* in McArdle, C. B., Ed., *Side Chain Liquid Crystal Polymers*, p. 69.

3 A. W. Hall, D. Lacey, J. S. Hill, K. M. Blackwood, M. Jones, D. G. McDonnell and I. C. Sage (1996) *Liquid Crystals*, **20**, 437-447.

3.6 Switching Results Of Polymers

Of all the polymers synthesised only one of them, polymer **7.8**, could be tested for ferroelectric switching. The other polymers which exhibited a SmC* phase where capable of switching, but did not give good enough alignment for measurements to be taken. The results of response time versus temperature are shown in table **3.6.1**.

70.0 Volts peak to peak, 250 mHz, square wave.

Table **3.6.1**

Temperature/°C	Time/ms
55	836
60	499
65	305
70	200
75	101
80	54

For a graph of response time versus temperature see figure **5.11**.

3.7 Mechanism Of Cyclopolymerisation

3.7.1 Why Cyclopolymerisation?

The main reasons to favour the cyclopolymerisation of the monomers in this study, rather than polymerisation by another mechanism (see **1.5**), are discussed as follows.

The principal requirement for cyclopolymerisation to proceed is the possibility of forming thermodynamically stable ring structures. The monomers in this study possess the correct structural requirements to cyclopolymerise to produce polymers incorporating unstrained alicyclic rings within the backbone [1,2].

The polymers produced are not crosslinked, as they are soluble in a variety of organic solvents, for example DCM and THF. Also, they do not possess any residual unsaturation as shown by ^{1}H NMR and IR spectroscopy.

Consider the thermodynamics of polymerisation [3]. The Gibbs free energy change for the polymerisation reaction, ΔG, is given by equation **3.7.1**.

$$\Delta G = \Delta H - T\Delta S \qquad \text{Equation } \mathbf{3.7.1}$$

The free energy of polymerisation must be negative for the reaction to occur. During the reaction there is a loss of entropy within the system because the monomers are free to move, whereas, once combined within the polymer backbone their degree of

freedom is much reduced. This large loss of entropy means that the $T\Delta S$ term is negative. For ΔG to be negative to allow reaction to occur, the ΔH term must be highly negative. This is the case, as the sp^2 carbon-carbon double bonding in the monomer is replaced by more efficient sp^3 carbon-carbon bonding in the polymer. However, when comparing monomers in this study with simple alkenes, the value of ΔH will be approximately twice as much, as each propagation step involves two double bonds, therefore strongly favouring cyclopolymerisation.

3.7.2 Ring Size of 1,4-Pentadienes and 1,6-Heptadienes

In this work there is the possibility for ring closure to give either five or six membered rings. It would be expected that propagation would proceed *via* the most energetically favourable route. This would mean head to tail addition of the radical to the double bond, resulting in a more stable secondary radical. In the case of the 1,4-pentadienes and the 1,6-heptadienes this would result in the formation of six membered rings. This is illustrated in figure **3.7.1**, using a 1,6-heptadiene as an example.

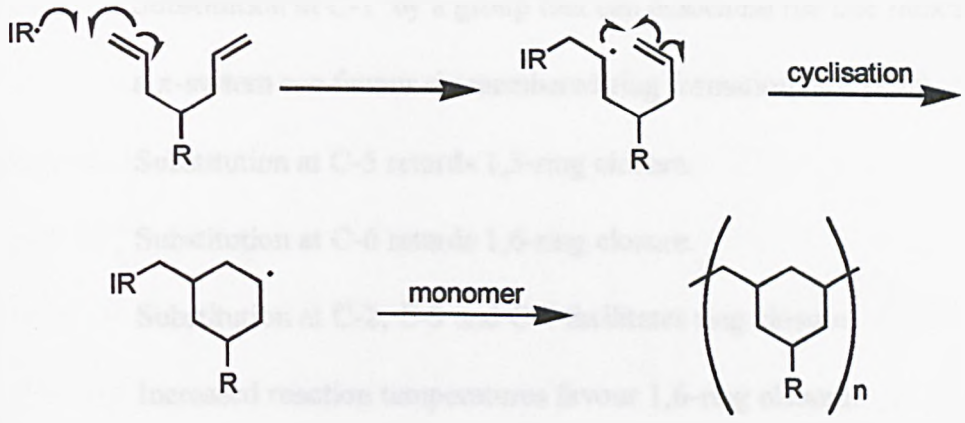


Figure **3.7.1**

However, it is suggested that all the monomers cyclopolymerise to form five membered rings. Evidence to support this suggestion can be given by examining the results obtained by the position of ring closure of substituted 5-hexenyl systems. These results can be compared to the monomers used in this work. Both the 1,6-heptadienes and the 1,4-pentadienes, after the first inter-molecular addition of monomer, can be viewed as 5-hexenyl systems [4]. The two possible modes of ring closure are illustrated in figure **3.7.2**.

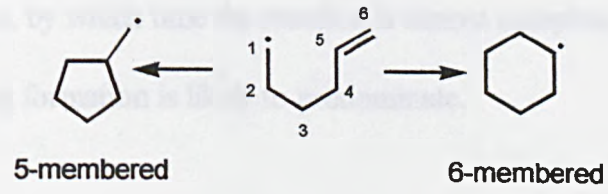


Figure **3.7.2**

The observations are summarised below.

Substitution at C-1 by a group that can delocalise the free radical into a π-system can favour six membered ring formation (see later).

Substitution at C-5 retards 1,5-ring closure.

Substitution at C-6 retards 1,6-ring closure.

Substitution at C-2, C-3 and C-4 facilitates ring closure.

Increased reaction temperatures favour 1,6-ring closure.

When compared to the simple system shown in figure **3.7.2** the 1,4-pentadiene and 1,7-heptadiene systems have no substituent at C-1 to delocalise the free radical, nor do they have substituents on C-5 or C-6 to affect the mode of ring closure. The 1,4-pentadienes are substituted at C-4 and the 1,6-heptadienes at C-5, both of which will help cyclization to occur. From these comparisons it is possible to favour the formation of five membered rings. However, with these simple di-allyl systems it has been found that ring size is kinetically controlled, with five membered rings being favoured at lower temperatures [1,2,5,6]. As the photo-initiated polymerisation is essentially carried out at or near room temperature (the highest temperature reached after thirty minutes, by which time the reaction is almost complete, is about 30 °C) five membered ring formation is likely to predominate.

This kinetic effect overrides the formation of the more thermodynamically stable six membered ring and also results in the formation of a less stable primary radical during the intramolecular cyclization process. The proposed mechanism for the

cyclopolymerisation of 1,6-heptadienes is shown in figure **3.7.3** and of the 1,4-pentadienes is shown in figure **3.7.4**.

1,6-Heptadienes

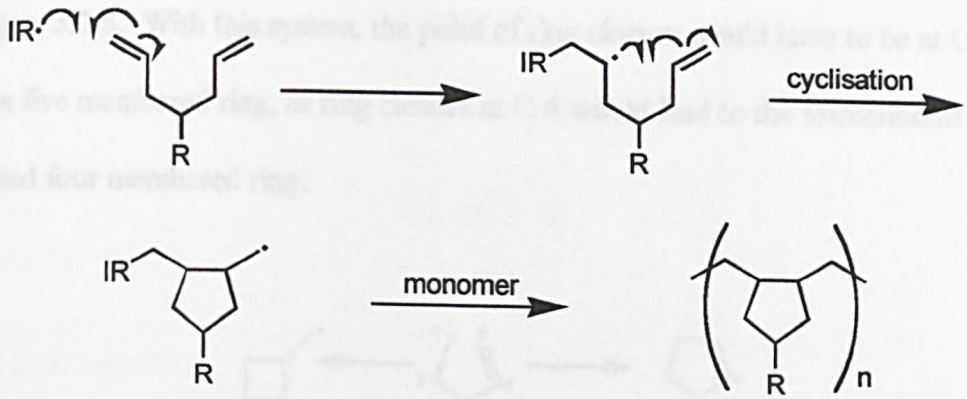


Figure **3.7.3**

1,4-Pentadienes

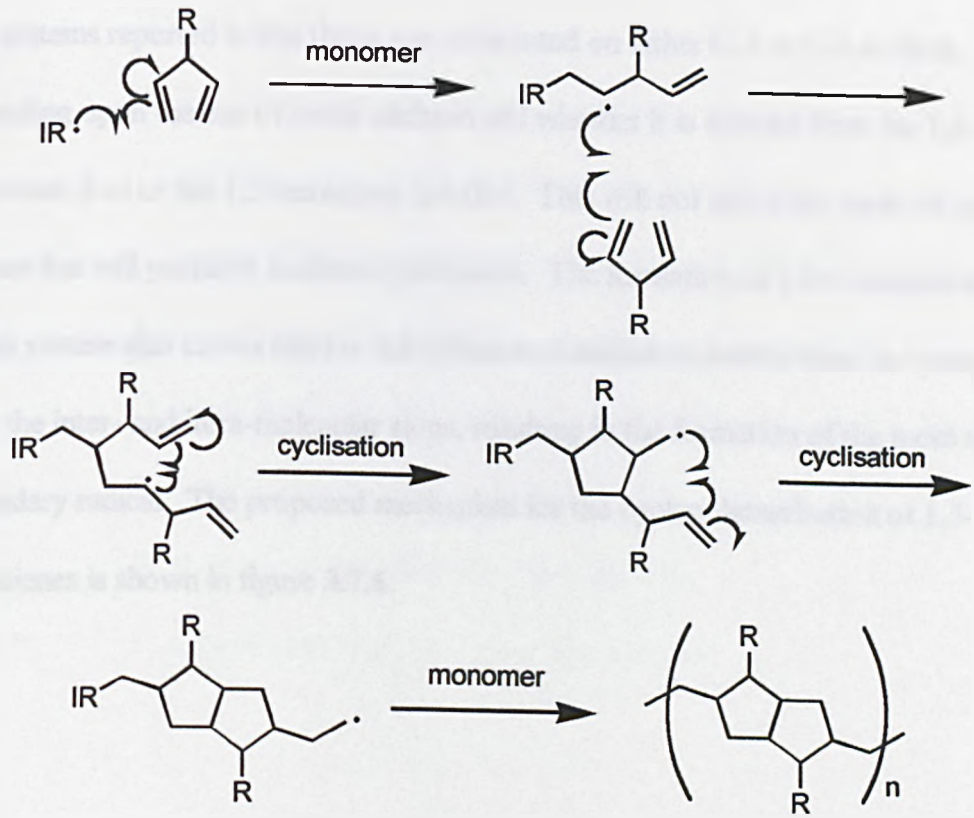
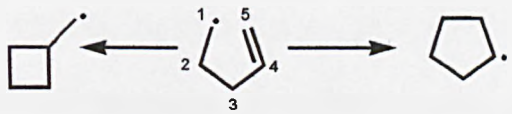


Figure **3.7.4**

3.7.3 Ring Size of 1,5-Hexadienes

The 1,5-hexadienes, assuming head to tail addition (see earlier), can be viewed as a substituted 4-pentenyl system. The two possible modes of ring closure are illustrated in figure **3.7.5**. With this system, the point of ring closure would have to be at C-5 to give a five membered ring, as ring closure at C-4 would lead to the formation of a strained four membered ring.



4-membered 5-membered

Figure **3.7.5**

The systems reported in this thesis are substituted on either C-2 or C-3 or both, depending upon the site of initial addition and whether it is derived from the 1,5-hexadiene-3-ol or the 1,5-hexadiene 3,4-diol. This will not affect the mode of ring closure but will probably facilitate cyclization. The formation of a five membered ring in this system also allows head to tail addition of radical to double bond to occur in both the inter- and intra-molecular steps, resulting in the formation of the more stable secondary radical. The proposed mechanism for the cyclopolymerisation of 1,5-hexadienes is shown in figure **3.7.6**.

1,5-Hexadienes

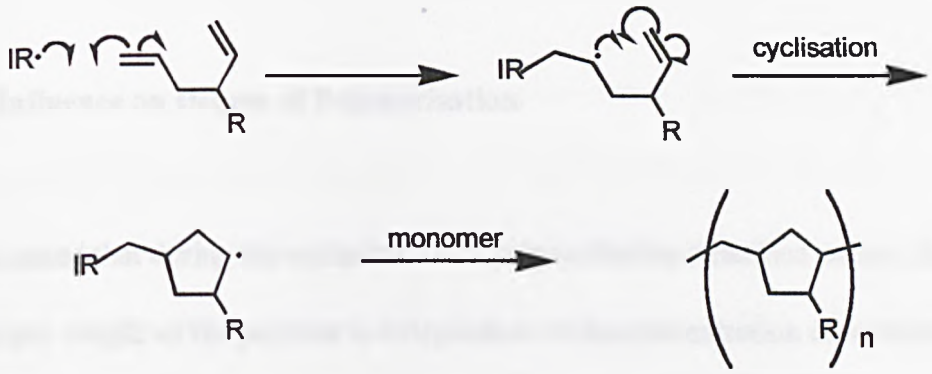


Figure **3.7.6**

3.7.4 References

1 G. B. Butler in *Comprehensive Polymer Science* (1989) ed. G. C. Eastman, A. Ledwith, S. Russo and P. Sigwatt, Pergaman Press, Oxford, p. 423.

2 G. B. Butler (1980) in *Polymeric Amines and Ammonium Salts*, ed. E. J. Geothals, Pergamon Press, Elmsford, New York, p. 125.

3 G. Odian (1991) *Principles of Polymerisation*, Wiley Interscience, New York, pp. 279-280.

4 G. Moad and D. H. Solomon (1995) *The Chemistry of Free Radical Polymerization*, Pergamon, p. 164.

5 G. B. Butler (1960) *J. Polym. Sci.*, **48**, 279.

6 P. J. Flory (1937) *J. Am. Chem. Soc.*, **59**, 241.

3.8 Mechanism Of Termination

3.8.1 Influence on Degree of Polymerisation

It was noted that during the optimisation of polymerisation described earlier, that the molecular weight of the polymer is independent of the concentration of initiator. The DP for most systems is also low. These two observations are indicative of termination by degradative chain transfer from monomer. As all these systems can be viewed as simple allylic systems, the most likely explanation for these observations is allylic hydrogen abstraction from the monomer by the growing polymer radical [1,2]. For a series of monomers with the same mesogen and spacer group the DP decreases in the order 1,4-polypentadiene, 1,5-polyhexadiene and 1,6-polyheptadiene.

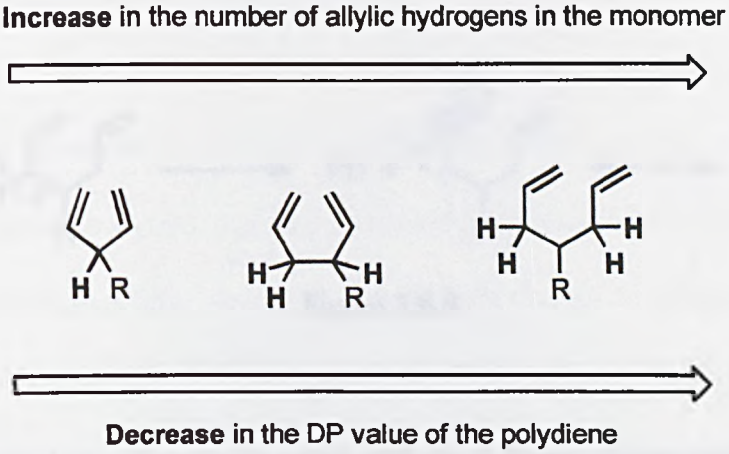


Figure **3.8.8**

3.8.2 Abstraction of Allylic Hydrogens

It can clearly be seen from figure **3.8.8** that the increase in the number of allylic hydrogens in the monomer is accompanied by a decrease in DP for the polymer. This observation also supports the theory, as the more allylic hydrogens there are in a monomer the more likely termination, rather than propagation, is to occur. This of course would lower the DP of the polymer. A likely mechanism by which this could occur is illustrated in figure **3.8.9** using a 1,6-heptadiene as an example. This figure shows the polymer radical, P·, abstracting an allylic hydrogen from the monomer, so generating a new free radical and an inactivated polymer, PH. The free radical is relatively stable, as it is resonance stabilised and not reactive enough to re-initiate polymerisation. The active centre is therefore removed from the reaction and probably destroyed by dimerisation of two allyl radicals.

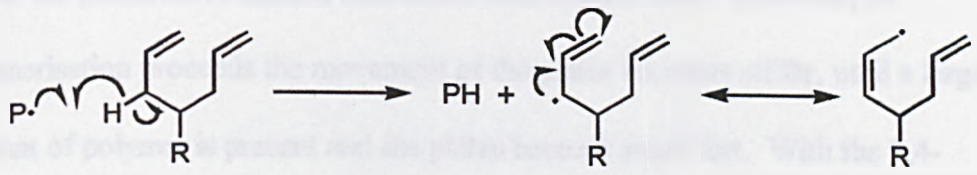


Figure **3.8.9**

A similar mechanism will probably occur with the 1,4-pentadienes and the 1,6-hexadienes to produce similar stable allyl radicals, as shown in figure **3.8.10**.

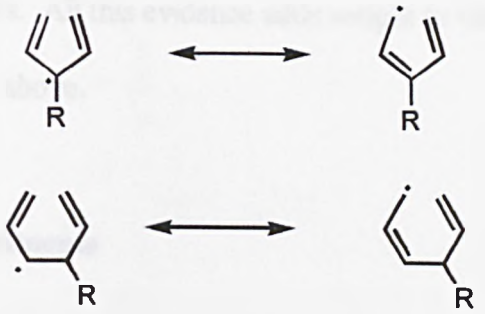


Figure **3.8.10**

3.8.3 Rate of Conversion of Monomer

Another significant observation is the relative rate of polymerisation. During the photopolymerisation process, the glass plate polymer 'sandwich' is periodically removed from the UV source to see how the reaction is going. The method used was to see if the glass plates could be slid past one another. At the beginning of the reaction, when the monomer is present as either a soft crystal, smectic or isotropic phase, the plates move against each other with relative ease. However, as polymerisation proceeds the movement of the plates becomes stiffer, until a large amount of polymer is present and the plates become stuck fast. With the 1,4-pentadienes this occurs after about ten minutes, with the 1,5-hexadienes it takes about thirty minutes and with the 1,6-heptadienes the plates will still slide past one another, even after two hours.

The chemical yield of polymer also shows a similar pattern. For a given mesogen and spacer the 1,4-pentadienes gave the highest yield, whereas the 1,6-heptadienes gave the lowest and the 1,5-hexadienes usually gave a yield which was intermediate

between that of the others. All this evidence adds weight to the mechanism for termination as described above.

3.8.4 Influence of Substituents

There is one problem that arises from the observations just described. Free-radical polymerisation of a C-C double bond is usually enhanced by substituents which can donate electron density to the propagating radical, either by inductive or mesomerical effects, thereby stabilising the radical and reducing the likeliness of termination occurring [1]. This is clearly contradictory to what is observed in this study. When the structure of the linking group between the diene moiety and the side chain (SC in figure **3.8.11**) is fully examined, the dipolar nature of the ester linking group will induce a partial positive charge to be produced inductively on the diene. This is shown in figure **3.8.11**, using a 1,4-pentadiene as an example.

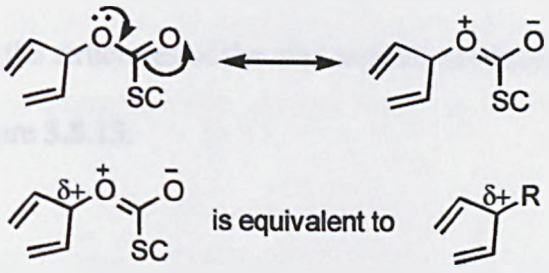


Figure **3.8.11**

Similar areas of partial positive charge are also produced with the other two dienes used in this study, as shown in figure **3.8.12**.

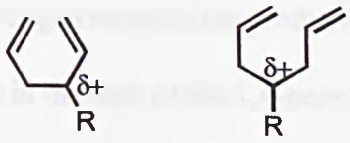


Figure **3.8.12**

These areas of positive charge should destabilise the propagating radical and hinder polymerisation. However, this clearly does not happen, as the monomers with both double bonds adjacent to the area of positive charge, the 1,4-pentadienes, clearly polymerise more quickly to a higher DP. The 1,5-hexadienes only have one double bond adjacent to the induced charge but they polymerise more slowly to give a lower DP. The 1,6-heptadienes have no double bonds adjacent to the area of positive charge, but these monomers take by far the longest to polymerise, and produce a very low DP. A possible explanation for the above observations could be as follows.

If the rate of polymerisation is relatively fast, then the rate of termination must be relatively slow and *vice versa*. Assuming the mechanism of termination described above is correct, then the structures of the allyl radicals produced by the different dienes is shown in figure **3.8.13**.

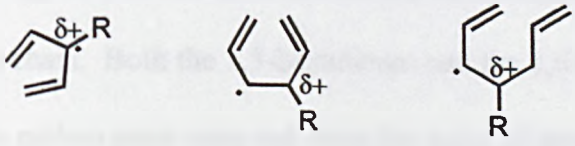


Figure **3.8.13**

If abstraction of an allylic hydrogen requires the production of a radical at the site of the partial positive charge, as in the case of the 1,4-pentadienes, it will be relatively de-stabilised and therefore harder to form in the first place. This will slow down the rate of termination relative to the rate of propagation, which will result in the quicker formation of polymers with a higher DP. Likewise, if abstraction of an allylic hydrogen can take place without removing one from the immediate area of the induced positive charge, then it will happen more easily. This will result in an increase in the rate of termination, resulting in slower polymerisation and polymers with a lower DP. This can be seen with the 1,5-hexadienes and 1,6-heptadienes, which have two and four more easily abstractable hydrogens respectively.

In contrast to the low DP of the poly-1,6-heptadienes in this study, the 1,6-diene shown in figure **1.5.7** gives polymers with a high molecular weight. This diene contains a quarternary nitrogen contained within the diene moiety, adjacent to both the carbons bearing the abstractable allylic hydrogens. This centre of positive charge would greatly reduce the stability of a radical produced by the abstraction of an allylic hydrogen, thereby suppressing termination and allowing a greater DP to be reached.

Another factor affecting the ease of abstraction of the allylic hydrogens is the steric hindrance of the side chain. Both the 1,5-hexadienes and the 1,6-heptadienes have allylic hydrogens one carbon atom removed from the point of attachment of the side chain, which would be more easily accessible, whereas the 1,4-pentadiene does not.

3.8.5 Low Degree of Polymerisation of Poly-1,6-Heptadienes

All this evidence supports the theory that termination is caused by abstraction of allylic hydrogens from monomer. However, there is one last point to consider. The 1,6-heptadienes do seem very reluctant to polymerise and when they do, yields and DP are usually quite low. A possible explanation could be due to timing of the termination step. For the other two dienes in the study, termination can only occur as an inter-molecular step. However, instead of the intra-molecular cyclization step of the 1,6-heptadienes, there is the possibility for termination to occur. As the molecular structure is such that an abstractable allylic hydrogen is the same distance away from the propagating radical as it is to the end of the carbon-carbon double bond, as shown in figure **3.8.14**. This would mean that there is the possibility for termination to occur much more often, resulting in slower polymerisation and a low DP, as observed.

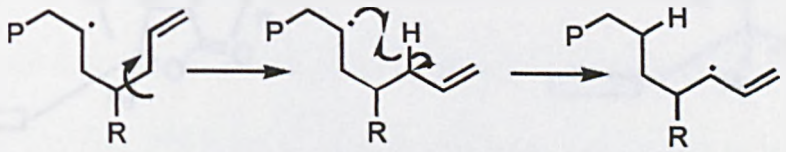


Figure **3.8.14**

3.8.6 References

1 G. Odian (1991) *Principles of Polymerisation*, Wiley Interscience, New York, pp. 279-280.

2 G. Moad and D. H. Solomon (1995) *The Chemistry of Free Radical Polymerization*, Pergamon, p. 164.

3.9 Further Evidence For cyclopolymerisation

Further evidence for the cyclic structures of the polymer backbone in these polydienes systems comes from some recent work that has been carried out at Hull on one of the intermediates we have used to prepare Baylis-Hillman SCLC polymers [1,2]. The intermediate alcohol was esterified with acrylic acid and the resulting monomer was then polymerised using the usual procedure, as shown in figure **3.9.1**.

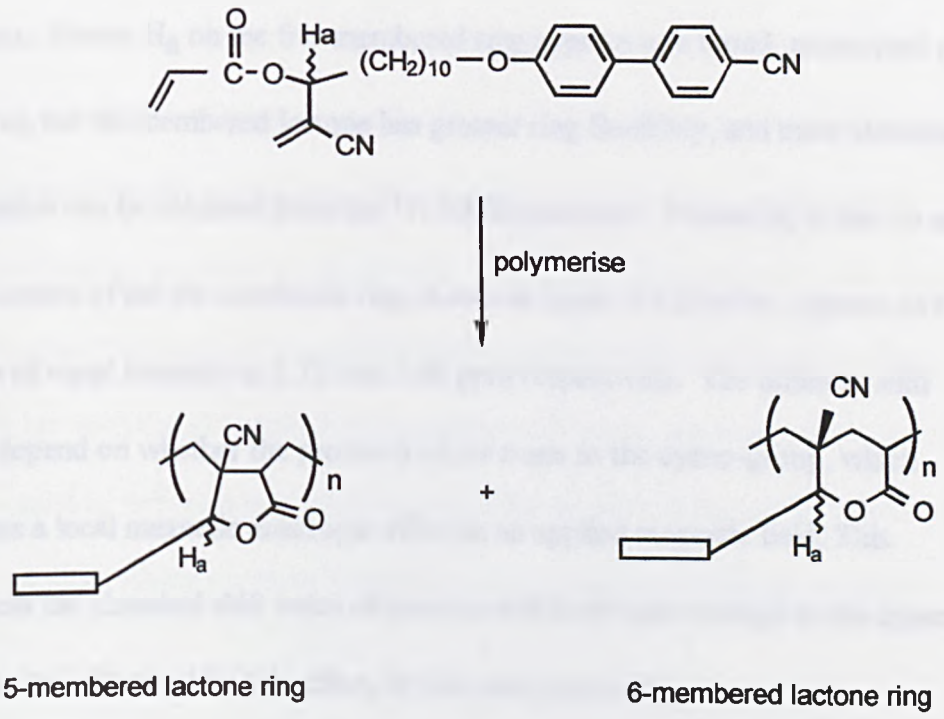


Figure **3.9.1**

The resulting product was a mixture of polymers, containing a 5-membered lactone, a 6-membered lactone and some cross-linked product [3].

Infrared spectroscopy shows two carbonyl absorptions at 1740 and 1685 cm^{-1} which correspond to the 5-membered and 6-membered lactone rings respectively. The carbonyl absorption for the 5-membered lactone ring is higher than that for the 6-membered lactone ring because of ring strain which reduces the normal carbonyl angle of 120 °C in the 5-membered ring.

The ^1H NMR (270 MHz) gives little information from which the structure of the polymers containing five membered rings can be deduced, due to the rigidity of such a structure. Proton H_a on the five membered ring appears as a broad, unresolved peak. However, the six-membered lactone has greater ring flexibility, and more structural information can be obtained from the ^1H NMR spectrum. Proton H_a in the *cis* and *trans* isomers of the six membered ring shown in figure **3.9.2** below, appears as two singlets of equal intensity at 3.75 and 3.60 ppm respectively. The different shift values depend on whether the proton is *cis* or *trans* to the cyano-group, which produces a local magnetic anistropic effect in an applied magnetic field. This influences the chemical shift value of protons which are near enough to the cyano-group to be influenced by this effect, in this case proton H_a.

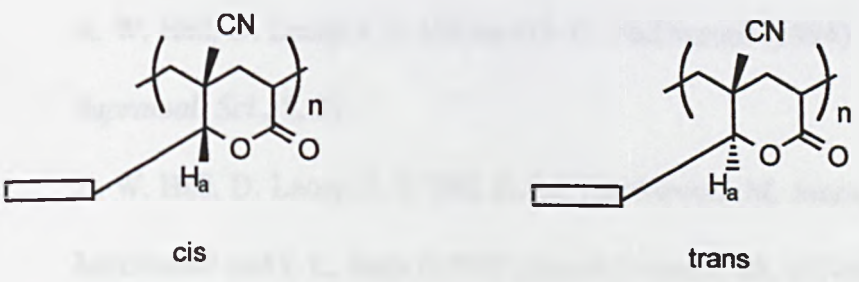


Figure **3.9.2**

This effect is not seen in the monomer, since the cyano-group is not fixed by the ring structure, so the unit to which the cyano-group is attached can rotate freely. The chiral centre to which proton H_a is attached is formed in the Baylis-Hillman reaction. Since this reaction produces racemic mixtures, only one peak in the ^1H NMR is seen for both isomers, as H_a exists in the same magnetic environment.

Photopolymerisation of the monomer in bulk also produced some cross-linked material which was insoluble in organic solvents such as DCM and THF. The reason why cross-linking could occur in this reaction and not in the other previously described cyclopolymerisations, was that the two alkenyl groups present in the Baylis-Hillman monomer differ slightly in reactivity, due to the different neighbouring activating groups, i.e. an ester and a nitrile. This led to some intermolecular reaction between alkenyl groups of the same reactivity, in preference to intra molecular reaction between the different alkenyl groups on the same monomer. Also, because the propagating radical is resonance stabilised by the adjacent group, it will have a longer life time, giving a greater possibility for intermolecular reaction to occur.

3.9.1 References

1 A. W. Hall, D. Lacey J. S. Hill and D. G. McDonnell (1994) *Supramol. Sci.*, **1**, 21.

2 A. W. Hall, D. Lacey, J. S. Hill, K. M. Blackwood, M. Jones, D. G. McDonnell and I. C. Sage (1996) *Liquid Crystals*, **20**, 437-447.

3 I. P. Buxton, A. W. Hall and D. Lacey (1997) *Macromol. Chem. Phys.*, **198**, 2307-2319.

3.10 Effect of Optical Isomerism on Polymerisation

As can be seen from the results obtained from the polymerisation of compound **1.2** its behaviour is markedly different from the behaviour of the other monomers studied. The only structural difference between compound **1.2** and the other monomers so prepared is the existence of not only (+) and (-) optical isomers, but also a *meso* isomer. This is due to the presence of the two chiral centres and symmetry. It could be argued that the difference in behaviour is explained simply by the presence of the two side groups and this could affect polymerisation directly, by steric hindrance for example. If it was just a simple matter of steric hindrance, this would impede propagation of the growing chain making termination more likely to occur, thereby producing shorter chains. However, this is clearly not the case as compound **1.2** produced by far the largest molecular weight polymer of any monomer in this study. Also, as described earlier, substitution on C-3 and C-4 facilitates ring closure during the cyclization step of polymerisation.

All polymers obtained from monomers other than compound **1.2** produced a normal distribution of molecular weight as expected, as shown by GPC. This also occurs with compound **1.2** for short reaction times, however as reaction time is increased a shoulder appears on the molecular weight distribution curve which, with sufficient reaction time, ultimately becomes completely bimodal (see figure **5.12**).

It is obvious from this observation that there are two mechanisms operating for the termination step. The molecular weight distribution that is obtained with short

reaction time is consistent with that produced by the other monomers. However the second peak corresponds to a polymer with a molecular weight almost an order of magnitude greater.

This difference could come about because of the preferential conformations which are adopted by the different isomers (see fig. **3.10.2**).

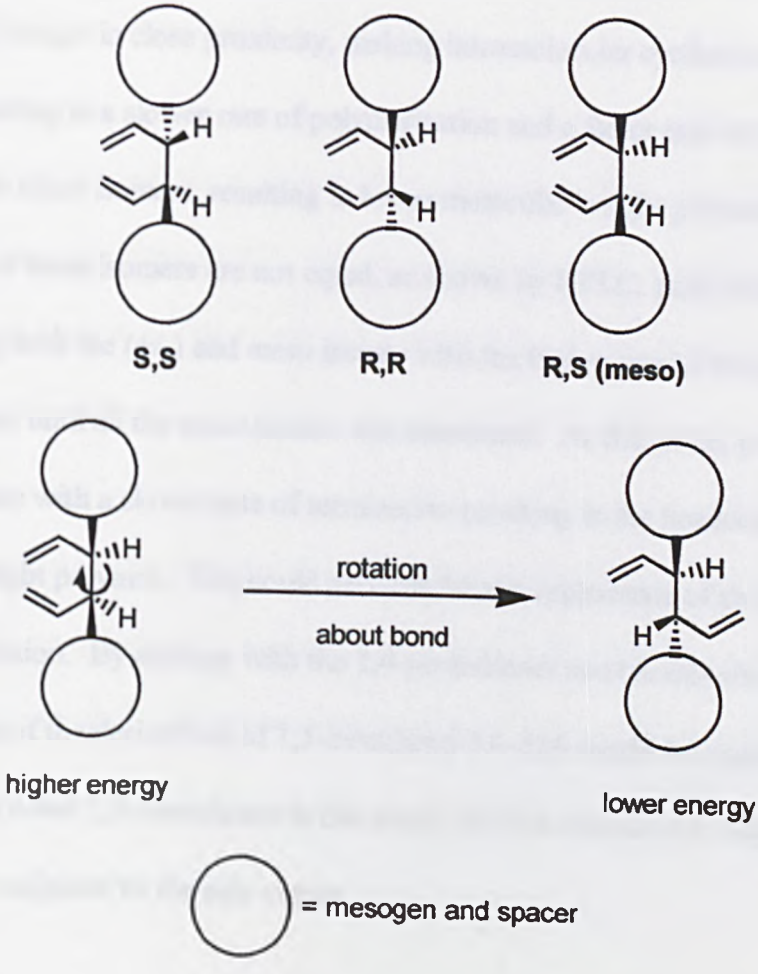


Figure **3.10.2**

Due to the nature of the side chains there will be two forces in operation; the steric repulsion that the large side chains will exert upon one another and the electrostatic

force produced by the permanent dipoles of the ester groups attaching the side chain to the diene. The side chains are likely to be on opposite sides of the molecule, as this will reduce the steric interactions and the dipoles of the reversed ester groups also cancel each other out. As can be seen the R,R and S,S optical isomers will probably adopt a conformation where both double bonds are in close proximity thereby making intramolecular cyclization occur more easily. However, if the *meso* isomer adopts a conformation with the side groups on opposite sides of the molecule, the double bonds are no longer in close proximity, making intramolecular cyclization more difficult, resulting in a slower rate of polymerisation and a faster rate of termination, relative to the other isomers, resulting in lower molecular weight polymers. As the proportions of these isomers are not equal, as shown by HPLC, polymerisation incorporating both the (+/-) and *meso* isomer with the higher rate of termination would proceed until all the *meso* isomer was consumed. At this point, polymerisation would continue with a slower rate of termination resulting in the production of higher molecular weight polymer. This could account for the appearance of the bimodal weight distribution. By analogy with the 1,4-pentadienes used in this study, the rate of termination of the derivatives of 1,5-hexadiene-3,4-diol would be expected to be lower than the other 1,5-hexadienes in this study, as both abstractable allylic hydrogens are adjacent to the side chains.

3.11 Routes to Polymers with a High Degree of Polymerisation

It was observed earlier that most of the polymers produced in this work have a DP which is low. As was discussed earlier, a high DP will give greater mesophase stability. Also, alignment properties of the polymers in a cell could also be improved when the DP is increased.

3.11.1 Resolution of Monomer 1.2

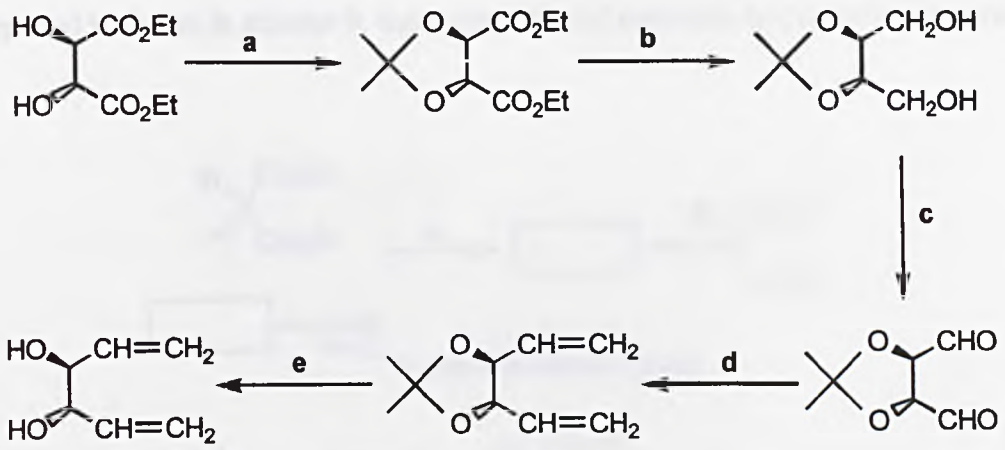
The first attempt involved the separation of the (+/-) isomers from the *meso* isomer of monomer**1.2** by preparative HPLC. The reasoning behind this approach was that the optically active isomers of this compound might polymerise to a high DP, as described earlier.

It was noticed that whilst determining the purity of this compound by HPLC prior to polymerisation, two peaks with markedly different retention times were observed. The column used was a C-18 reversed phase column, eluted with acetonitrile. One peak had a retention time of ≈ 16 minutes, and the other ≈ 18 minutes, with relative quantities of aproximately 2:3.

Unfortunately, when this system was scaled up for preparative HPLC the separation of the two peaks was insufficient to allow purification of one or both of the isomers. A number of solvent combinations was then tried, but efficient separation resulted in very long retention times, which made the procedure impractical to carry out.

3.11.2 Synthesis of a Chiral Isomer of 1,5-Hexadiene-3,4-diol

Since separation of the monomer proved unsuccessful, it was decided to attempt the synthesis of one of the chiral isomers (S,S) of 1,5-hexadiene-3,4-diol, using (+)-diethyl tartrate as a chiral starting material, as shown in scheme **8**.



a 2,2-Dimethoxypropane, THF (dry), Amberlyst 15 H^+.

b Lithium aluminium hydride, THF (dry).

c Pyridinium dichromate, DCM (dry).

d Methyltriphenylphosphonium bromide, sodium hydride, dimethyl sulphoxide.

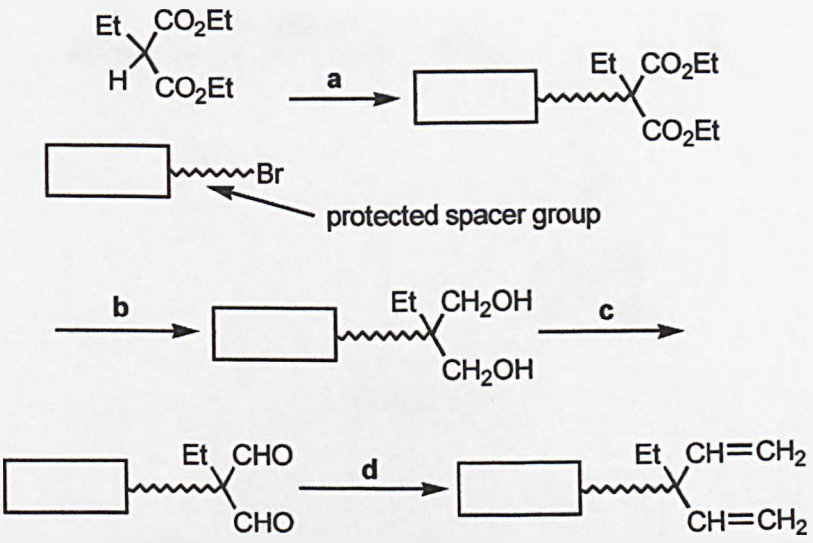
e THF, water, Amberlyst 15 H^+.

Scheme **8**

Unfortunately, this synthesis failed at step **c**, the oxidation of the diol to the dialdehyde, presumably because of the close proximity of the two functional groups.

3.11.3 Synthesis of Monomers with No Allylic Hydrogens

The next step was to attempt the synthesis of a monomer without any allylic hydrogens. This would prevent degradative chain transfer to monomer by allylic hydrogen abstraction. The simplest system to attempt would be a 1,4-pentadiene, as they have the least allylic hydrogens to start with. The proposed synthesis of such a compound is shown in scheme **9**, using ethyl diethyl malonate as the stating material.



Scheme **9**

a Sodium ethoxide, ethanol.

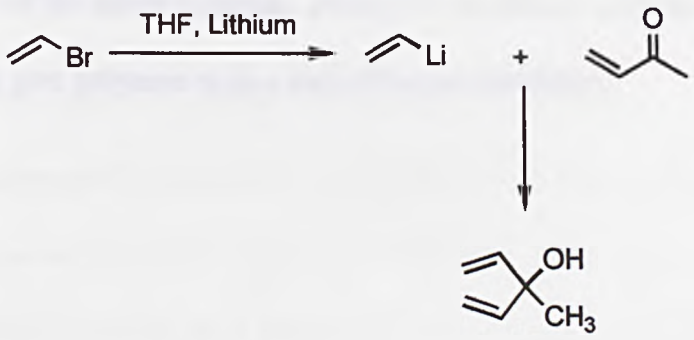
b Lithium aluminium hydride, diethyl ether (dry).

c Pyridinium dichromate, DCM (dry).

d Methyltriphenylphosphonium bromide, sodium hydride, dimethyl sulphoxide.

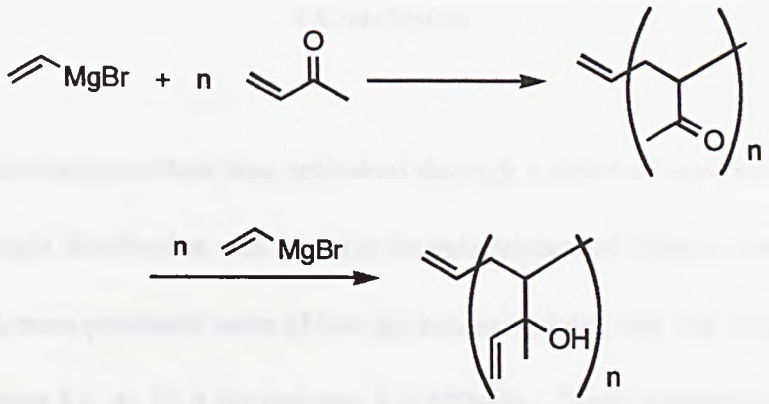
However, this synthesis also failed at step **c**, the oxidation of the diol to the dialdehyde, presumably for the same reasons as in scheme **8**.

Due to the failures of the routes described above, a synthesis which does not involve oxidation or reduction of an intermediate was devised. The synthesis of 3-methyl-1,4-pentadiene-3-ol was to be attempted using vinyl lithium and methyl vinyl ketone is shown in sceme **10**.



Scheme **10**

Vinyl lithium proved difficult to synthesise by the route described above, so vinyl magnesium bromide was used instead. Unfortunately, this resulted in the Michael addition of the vinyl magnesium bromide to the methyl vinyl ketone which resulted in the polymerisation of the methyl vinyl ketone, followed by the addition of the remaining vinyl magnesium bromide to the polyketone, to yield the polymer as shown in scheme **11**. Evidence from ^{1}H NMR and IR spectroscopy support the proposed structure of the polymer.



Scheme 11

After the failure of the above synthesis, attempts to synthesise monomers which would hopefully give polymers with a high DP were abandoned.

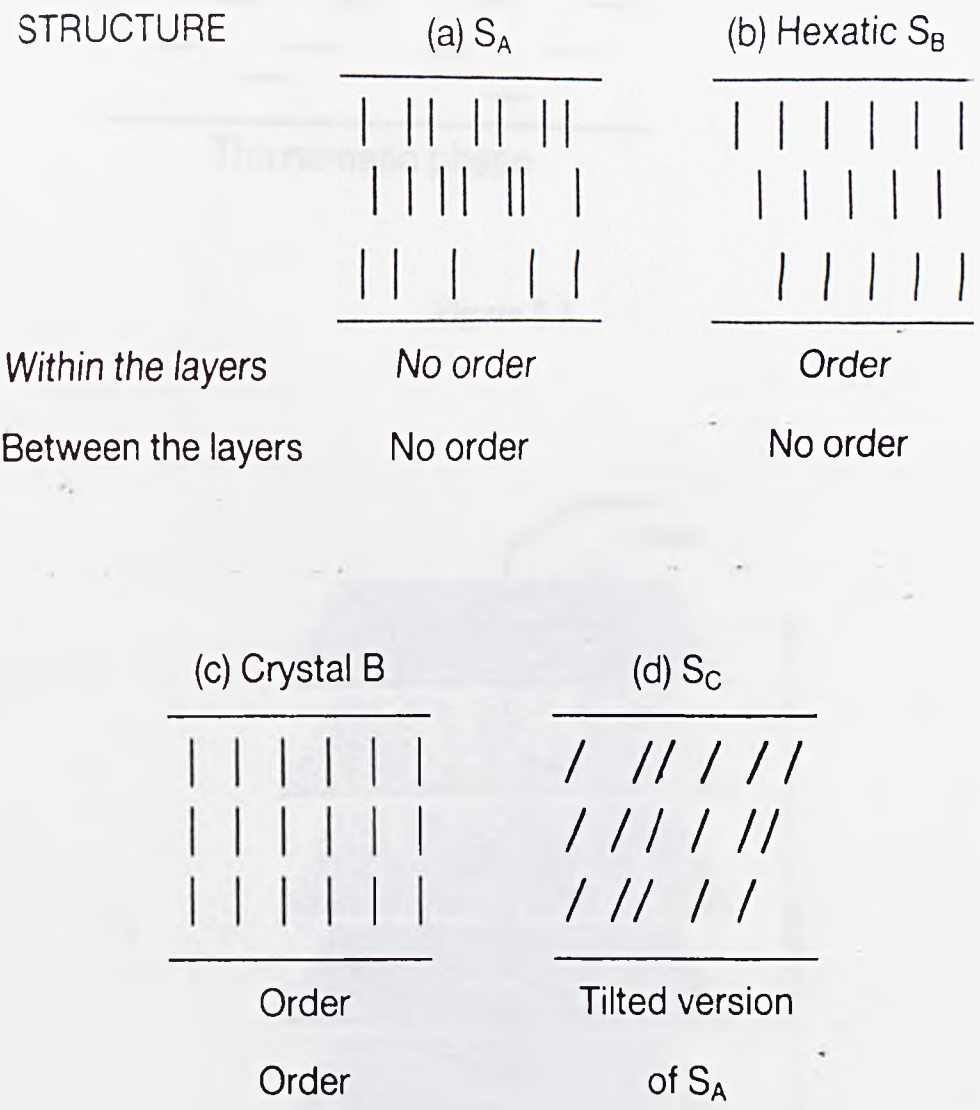
4 Conclusion

The polymerisation procedure was optimised through a series of experiments. The molecular weight distribution was found to be independent of initiator concentration and most polymers produced were of low molecular weight, with DP ranging from 5.51 for polymer **5.6**, to 25.4 for polymer **1.2-120min**. These observations and the nature of the monomers involved, led us to believe that the factor limiting molecular weight was degradative chain transfer to monomer by allylic hydrogen abstraction.

It was thought that the low molecular weight of the polymers led to difficulties in achieving alignment good enough, with the exception of polymer **7.8**, for ferro-electric switching studies to be undertaken. Attempts to synthesise monomers without any allylic hydrogens, in an attempt to obtain polymers of a higher molecular weight, proved to be unsuccessful. However, a polymer system was synthesised which added evidence to support the proposed structures of the polymers and the mechanism of cyclopolymerisation.

All the polymers synthesised, apart from polymers **6.4** and **6.5**, possess a liquid crystalline phase. All the polymers with two phenyl rings in the side chain, series **1** to **4**, exhibited the SmA phase, with ranges from 8.6 °C for polymer **3.8**, to 128 °C for polymer **1.2-120min**. All the polymers with three phenyl rings in the side chain, series **5** to **7**, with the exception of polymers **6.4** and **6.5**, exhibited the SmC* phase, with ranges from 56.6 °C for polymer **7.11**, to140.9 °C for polymer **5.4**.

The glass transitions of the polymers occurres near to room temperature, making them potentially useful in display devices, if they exhibit the correct phases and alignment difficulties could be overcome.



Simple representation of a selected number of smectic phases.

Figure 5.1

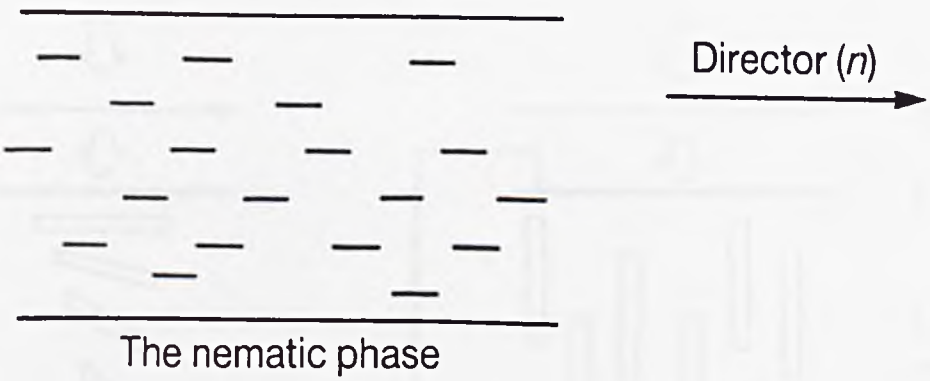
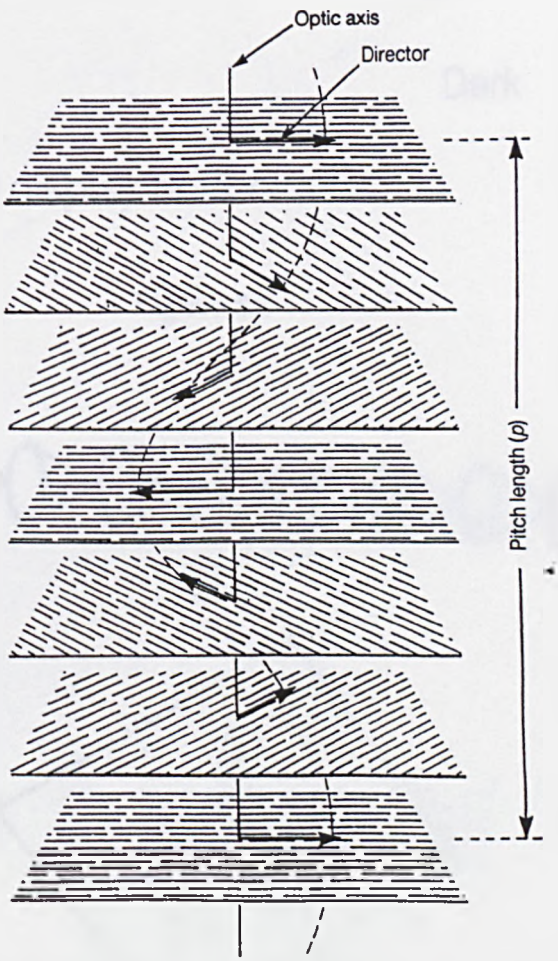
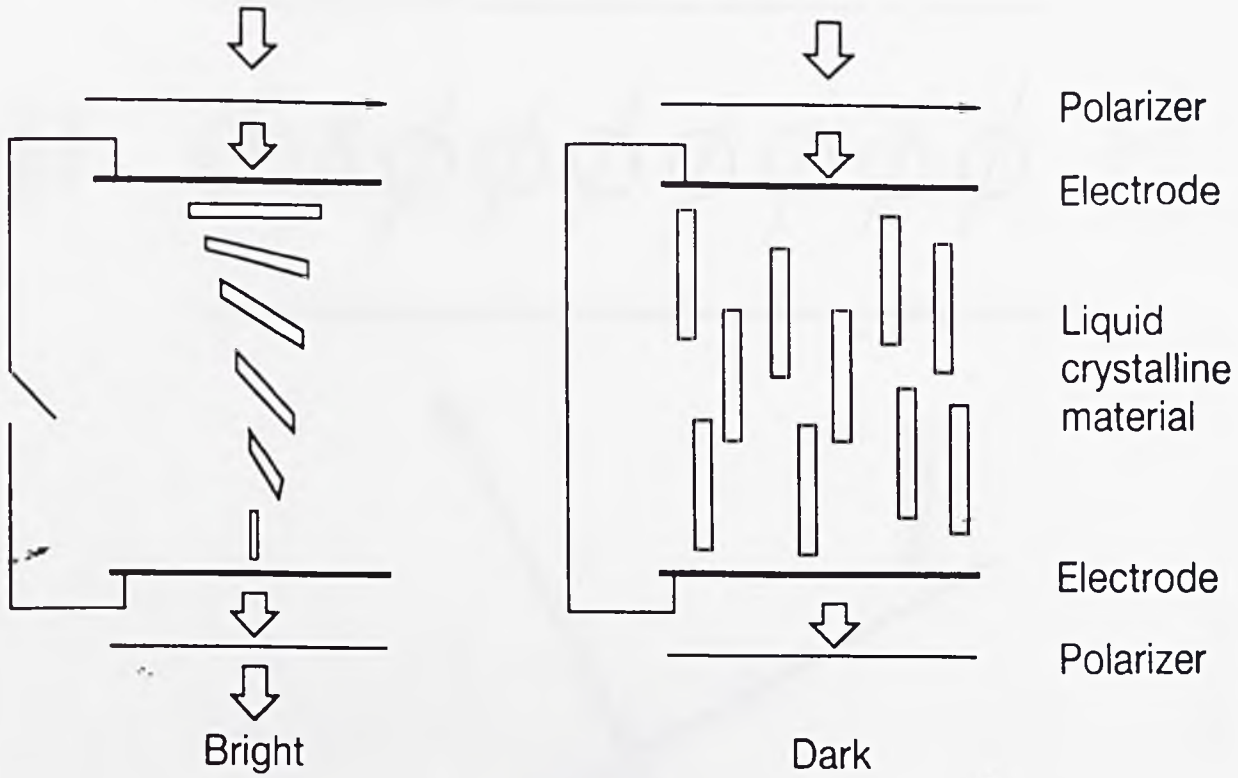


Figure 5.2



The helical structure of the cholesteric (chiral nematic) phase.

Figure 5.3



The twisted nematic display device.

Figure 5.4

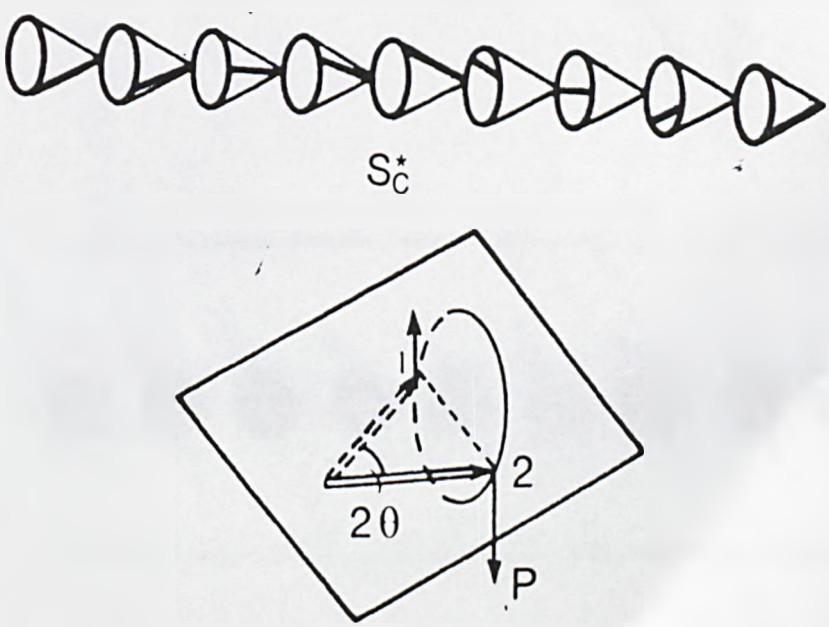


Figure 5.5

'Up'
state
θ
'Down'
state
θ
Polarizer
Analyzer
Dark
'off' state
Bright
'on' state

Figure 5.6

Curve 1: DSC
File info: jhpb2rpt Thu May 9 10:30:00 1996
Sample Weight: 5.910 mg

monomer 1.2

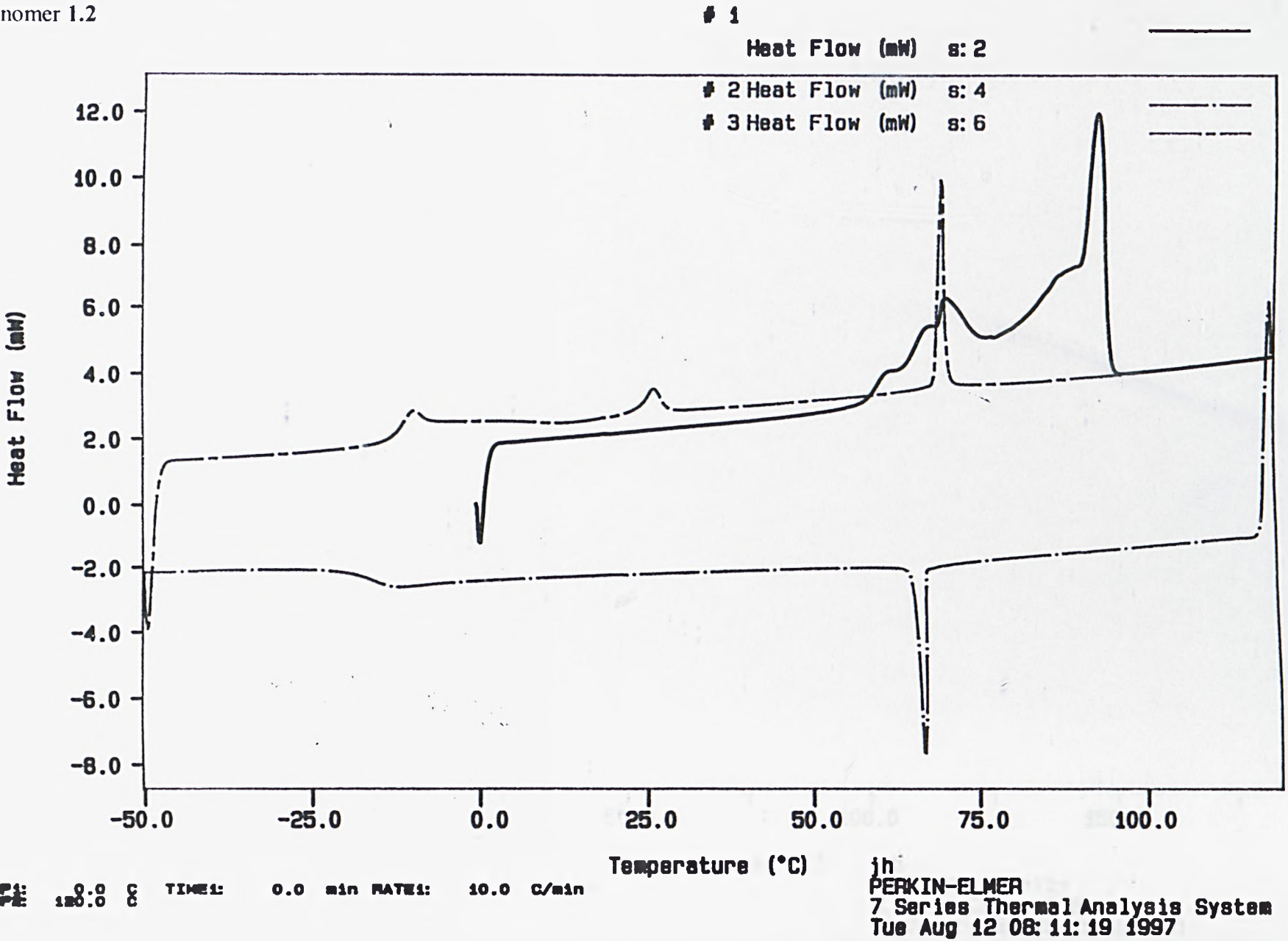
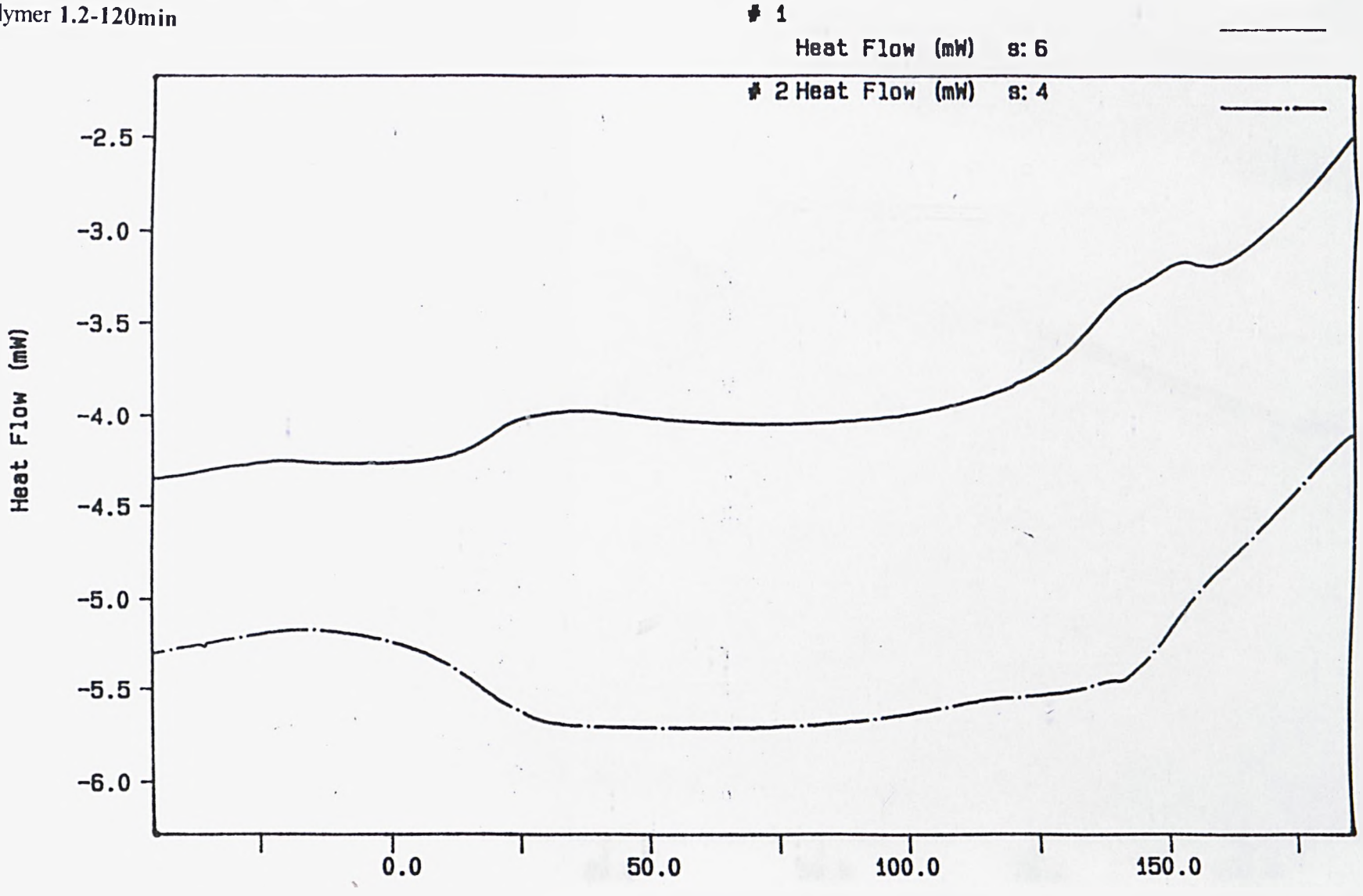


Figure 5.7

Curve 1: DSC
File info: pb30a Wed Apr 5 14:10:18 1995
Sample Weight: 5.030 mg

polymer 1.2-120min



TEMP1: -50.0 C TIME1: 0.0 min RATE1: 10.0 C/min
TEMP2: 150.0 C

pb
Hull University
Liquid Crystal Group
Wed Apr 5 14:41:14 1995

Figure 5.8

Curve 1: DSC
File info: pb136 Fri Jul 18 03:51:51 1997
Sample Weight: 5.270 mg

monomer 5.6

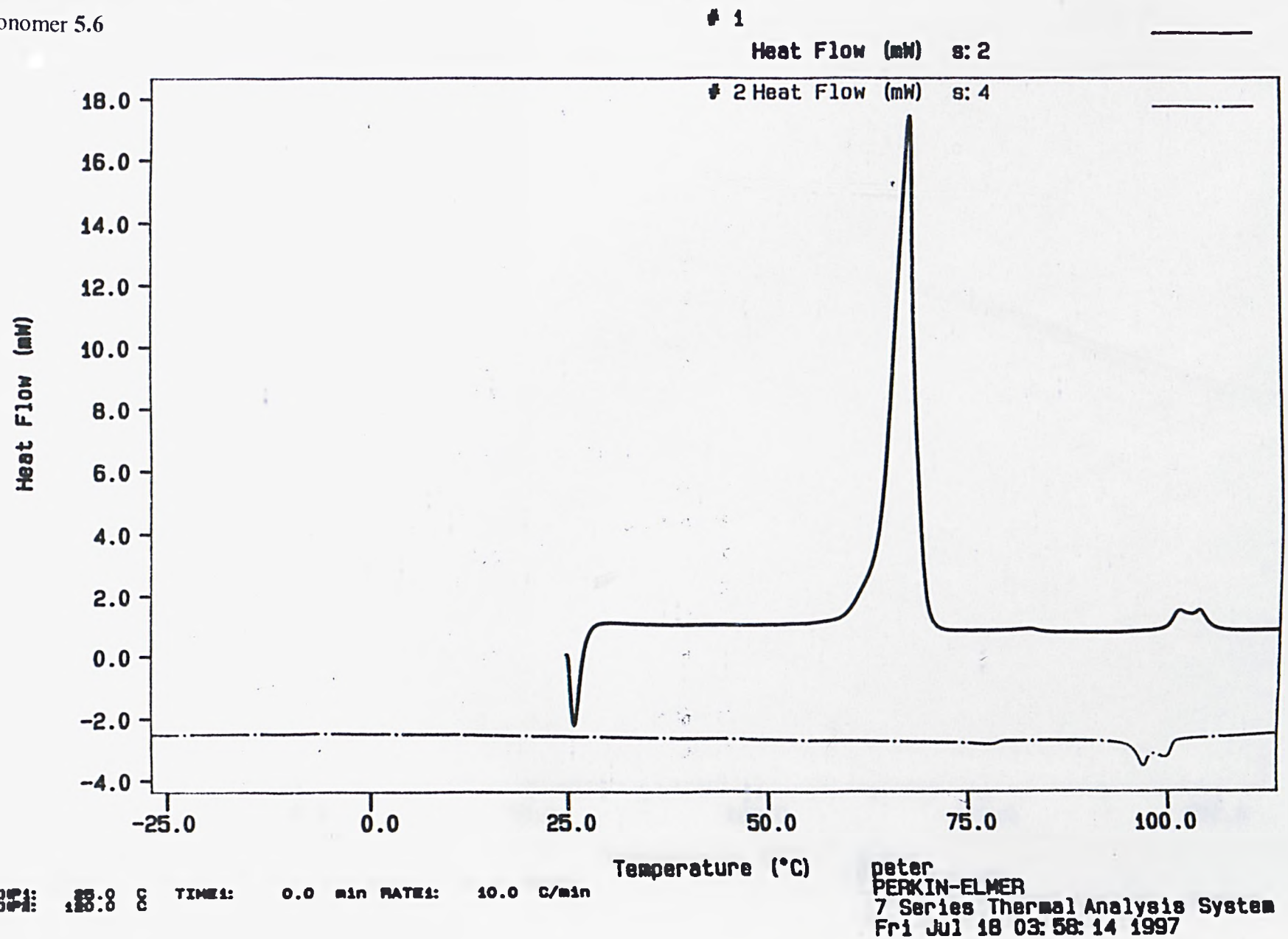


Figure 5.9

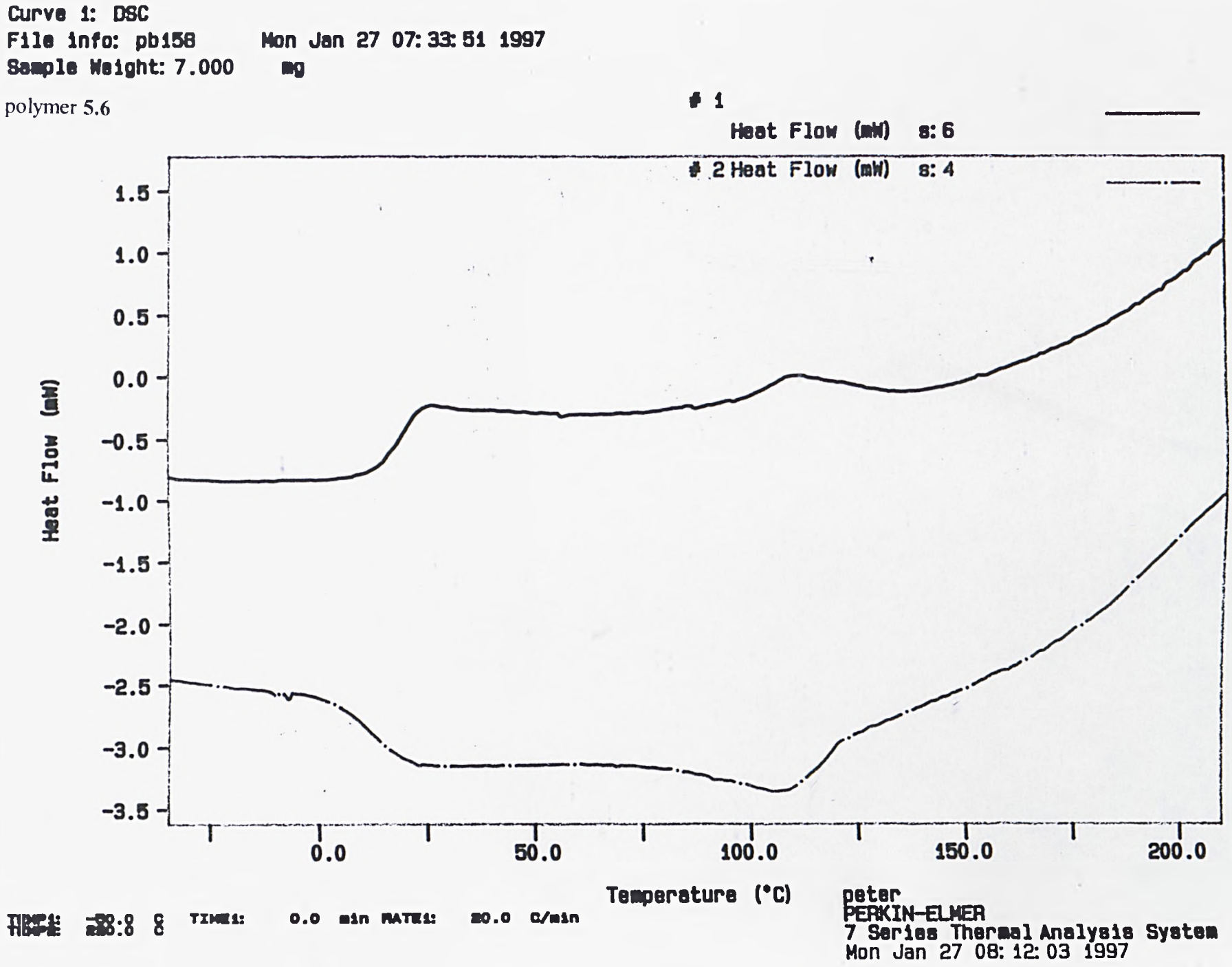
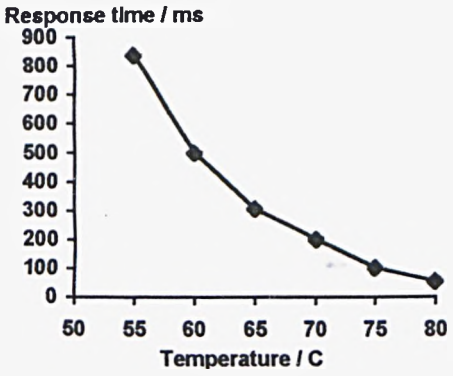
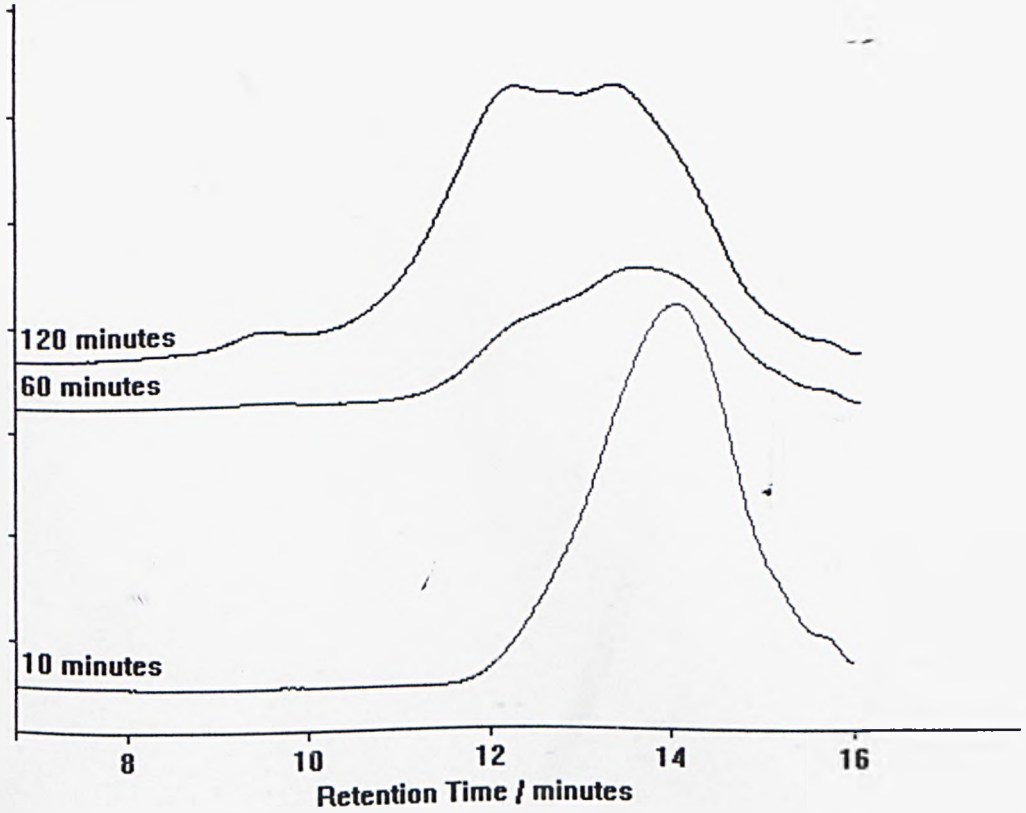

Curve 1: DSC
File info: pb158 Mon Jan 27 07:33:51 1997
Sample Weight: 7.000 mg
polymer 5.6
1
Heat Flow (mW) s:6
2 Heat Flow (mW) s:4
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
Heat Flow (mW)
0.0
50.0
100.0
150.0
200.0
Temperature (°C)
TIME1: 0.0 min RATE1: 20.0 C/min
peter
PERKIN-ELMER
7 Series Thermal Analysis System
Mon Jan 27 08:12:03 1997

Figure 5.10



Graph of response time for switching of polymer **7.8**.

Figure **5.11**



Molecular weight distibutions of polymers from series **1**.

Figure **5.12**