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T. E. Mann; D. Lacey

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The effect of molecular structure on the thermal properties of ferroelectric liquid crystalline cyclic siloxane tetramers

T. E. MANN
PETA Solutions, Perkin Elmer, Chalfont Road, Seer Green,
Beaconsfield HP9 2FX, UK

and D. LACEY*
Department of Chemistry, Faculty of Science and the Environment,
University of Hull, Hull HU6 7RX, UK

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A series of liquid crystalline cyclic siloxane tetramers was prepared to investigate, in a systematic manner, the role of molecular structure of (a) the spacer group, (b) the mesogenic side group and (c) the chiral end group, on the liquid crystalline behaviour of these novel tetramers. The results from this systematic structure/property correlation study clearly showed the effects of the structure of the chiral end group and the mesogenic side group on the thermal stability and temperature range of the SmC* phase (ferroelectric) exhibited by these materials. For a given chiral end group, the effect of the length of the spacer group on the thermal stability and temperature range of the SmC* phases depended greatly on the structure of the mesogenic side group. By appropriate choice of spacer group, mesogenic side group and chiral end group, a number of tetramers exhibiting wide SmC* ranges (ferroelectricity) from below room temperature were synthesized.

1. Introduction

Since the first introduction of side group liquid crystalline (SGLC) polymers by Finkelmann in 1977 there have been many studies in this area into (a) the effect of the molecular structure of the polymer backbone, spacer group and mesogenic side group on the thermal and physical properties of these polymers, and (b) the applications of such polymers in the area of ferroelectric display devices [1–4], non-linear optics [5–7], optical data storage [8, 9], pyroelectric detectors [10, 11], etc.

A substantial number of polymer backbones for SGLC polymers have been used, the most common being poly(acrylates), poly(methacrylates), poly(siloxanes) and poly(ethers). Recently, great care has been taken in producing SGLC polymers with well defined degrees of polymerization (DP values) and distribution of the molecular masses (M_w/M_n values) [12–14]. This has enabled a more precise study to be undertaken to establish the role of molecular structure on the thermal and physical properties of SGLC polymers.

However, one interesting area in SGLC polymer studies which has been somewhat neglected is the subject of cyclic SGLC polymers, even though they have been shown to be useful materials for optical data storage devices [15], optical filters [16] and reversible holographic-optical data storage devices [17]. It has been suggested [18, 19], because of the structural similarity of these cyclic polymers to both calamitic and discotic liquid crystalline materials, that cyclic SGLC polymers could exhibit both calamitic and discotic phases. With the appropiate structural features, these systems could exhibit a uniaxial (rod-based nematic phase) to biaxial (discotic nematic phase) transition and therefore cross the boundaries between the optical properties of the calamitic and discotic systems. Besides our original work in this area in comparing the thermal properties of cyclic and linear polysiloxanes [20] and the studies of Kreuzer [18] (cyclic homo- and co-polysiloxanes) and Bunning [19, 21] (X-ray studies), very little research work has been carried out on these interesting polymeric systems. In this paper we detail our systematic approach to investigate the effect of molecular structure of (a) the spacer group, (b) the mesogenic side group core and (c) the chiral end group, on the thermal properties of liquid crystalline cyclic siloxane tetramers of the structure **1**. Mesogenic side groups containing a chiral moiety were selected on the premise that such polymers incorporating these mesogenic side chains would exhibit either chiral

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*Author for correspondence;
e-mail: D.Lacey@chem.hull.ac.uk

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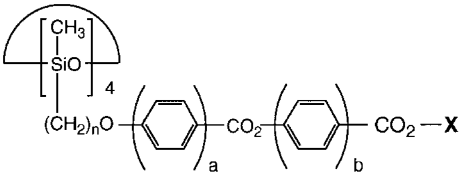


n = 6 or 11; a, b = 1 or 2.
X = $CH_2\overset{*}{C}H(CH_3)C_2H_5$ or $\overset{*}{C}H(CH_3)C_6H_{13}$.

Structure 1.

nematic or chiral SmC phases. Such polymers would be useful for either optical filters (chiral nematic phase) or ferroelectric display devices (chiral smectic C phase).

2. Results and discussion

The results from this investigation on liquid crystalline (LC) cyclic siloxane tetramers can be conveniently divided into two sections. Section 2.1 details the effect of the molecular structure of the monomeric mesogenic side group precursor on their LC behaviour, whilst a similar, but more detailed, study on the corresponding cyclic siloxane tetramers is outlined in § 2.2.

2.1. *Monomeric precursors of the mesogenic side groups*

A schematic representation of the structure of the mesogenic side group used in this study is given in the figure, which clearly shows the three different features of the side group which will be used to investigate the role of molecular structure on the thermal properties of the mesogenic side group precursors.

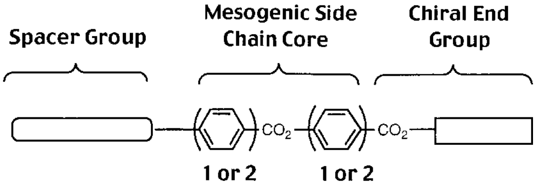


Figure. A schematic representation of the structure of the mesogenic side group.

The results from our work on the monomeric mesogenic side chain group precursors can be subdivided into two sections, depending on the structure of the chiral end group used.

2.1.1. *The 2MB series*

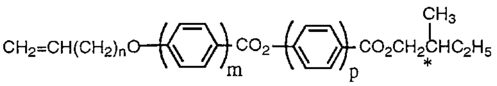
The structures of the compounds in the 2MB series, along with their melting points and transition temperatures are given in table 1. All the compounds in the 2MB Series contain an (*S*)-(−)-2-methylbutyl (2MB) chiral end group.

All the side group precursors (**4e–h** and **4m–p**) contain a terminally positioned alkenyl group which was used to attach the mesogenic side chain to the subsequent cyclic tetramer backbone. They generate, therefore, an effective alkyl spacer length of 6 ($n = 4$) or 11 ($n = 9$) carbon atoms.

It can be seen from the data given in table 1, that there is a marked change in the mesophase thermal stability as the number of phenyl rings is altered in the core of the mesogenic side chain.

2.1.1.1. *Short spacer group (n = 4).* Compound **4e**, which contains two phenyl rings was the only compound that did not exhibit the SmC* phase in the 2MB Series. The addition of a further phenyl ring in the core near to the chiral end group, compound **4f**, gave a marked increase in both the melting and clearing temperatures and the introduction of a SmC* phase. The increase was 62°C for the melting temperature and 120°C for the clearing temperature. The mesogenic thermal stability of the system was drastically increased by the addition of a fourth phenyl ring to the core (**4h**). As a consequence of this, an N* phase was introduced. This increase can be attributed to the overall increase in the size of the mesogenic core.

Table 1. The melting points and transition temperatures (°C) for monomers containing the (*S*)-(−)-methylbutyl (2MB) chiral moiety.



Mesogenic side group	*n*	*m*	*p*	Mesophases exhibited
4e	4	1	1	Cr 22.1 SmA 46.7 I
4f	4	1	2	Cr 84.0 SmC* 154.7 SmA 166.6 I
4g	4	2	1	Cr 85.6 SmC* 107.8 SmA 189.7 I
4h	4	2	2	Cr_1 105.1 Cr_2 113.3 SmC* 181.6 SmA 292.6 N* 307.7 I
4m	9	1	1	Cr 45.8 SmC* 51.3 I
4n	9	1	2	Cr 67.9 SmC* 104.3 SmA 151.4 N* 153.5 BP 155.1 I
4o	9	2	1	Cr 50.2 SmC* 128.8 SmA 171.6 I
4p	9	2	2	Cr_1 72.5 Cr_2 104.4 SmC* 225.2 SmA 288.0 I

The introduction of a phenyl ring in the core near to the spacer group, compound **4g**, also leads to an increase in both the melting and clearing temperatures of the mesogen. The increase in the melting temperature over the two ring system was 64°C and for the clearing temperature, 143°C. This again was expected due to the increase in the size of the mesogenic core.

The arrangement of the three phenyl rings in compounds **4f** and **4g** had a marked effect on the thermal stabilities of the SmC* and SmA phases exhibited. When the biphenylyl moiety contained the chiral end group (compound **4f**), this compound gave the highest SmC* thermal stability (47°), but the lowest SmA thermal stability (23°). This resulted in **4f** exhibiting a wide SmC* range (71°), whereas **4g** exhibited a wide SmA range (82°). Both compounds had similar melting points.

The introduction of a fourth phenyl ring into the core structure giving compound **4h**, effectively forming a twin biphenylyl core, led to a very large increase in both the melting and clearing temperatures. The melting temperature was found to be over 100°C and the clearing temperature over 300°C, a difference of 118°C over **4g**. In addition to the SmC* and the SmA phases, **4h** also exhibited a crystal–crystal transition but, more importantly, a narrow chiral nematic phase (15°).

2.1.1.2. *Long spacer group* ($n = 9$). On increasing the length of the spacer group from 6 (for example, compound **4h**) to 11 (for example, compound **4p**) carbon atoms, the melting points and the thermal stabilities of the SmA phases were decreased but the thermal stabilities of the SmC* phases increased. The only exception to this was compound **4n**. Although the melting point for this compound was lower than its analogue with a shorter spacer group (**4f**), the thermal stabilities for both the SmC* and SmA phases decreased. With regard to the SmC* phase, a decrease of 50° was observed. The liquid crystalline behaviour for this compound was very different from the other seven members of the series, and indeed from the eight members of the following 1MH Series, in that it was the only compound to exhibit a Blue Phase and one of only two compounds to exhibit a chiral nematic phase. For both the 2MB and 1MH series, the predominant mesophases were the SmC* and SmA phases.

The compound incorporating two biphenylyl units, compound **4h** with a short spacer group exhibited a narrow range chiral nematic phase, whereas compound **4p** exhibited SmC* and SmA phases only. Compound **4p** in fact exhibited the widest SmC* range (121°) of all the compounds both in the 2MB and the following 1MH Series.

2.1.2. *The 1MH series*

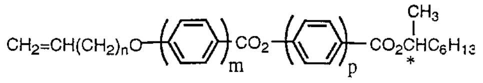
The structures of compounds in the 1MH Series, along with their melting points and transition temperatures are given in table 2. All the compounds in the 1MH series contain an (*R*)-(+)-1-methylheptyl (1MH) chiral end group.

The most striking difference in the liquid crystalline behaviour between compounds containing a chiral 1-methylheptyl end group and those containing a chiral 2-methylbutyl end group is that the introduction of the 1-methylheptyl group significantly lowers both the melting point and the thermal stabilities of the SmC* and SmA phases, although compound **4a** exhibits a SmC* phase, whereas its analogue, compound **4e**, exhibited a SmA phase. None of the compounds in the 1MH series exhibited a chiral nematic or a Blue Phase.

For compounds containing three phenyl rings in their structures, compounds **4b**, **4c**, **4j** and **4k**, in all cases where these molecules had the biphenylyl unit containing the chiral end group, the SmC* and SmA had lower thermal stabilities. This fact was only true in the 2MB Series where the compounds had a spacer group containing 11 carbon atoms (**4o** and **4p**); with a shorter spacer group, compound **4f** had the higher SmC* thermal stability.

The previous trend found for the 2MB series whereby compounds of higher SmC* and lower SmA thermal stability arose on increasing the length of the spacer group, was also found to be true for the 1MH series, except for compound **4i**, which did not exhibit liquid crystalline behaviour. Also, both the 4-ring compounds gave very wide range SmC* and SmA phases, with compound **4d** exhibiting a wide SmA range (139°) and compound **4l** a wide SmC* range (70°).

Table 2. The melting points and transition temperatures (°C) for monomers containing the (*R*)-(+)-methylheptyl(2MH) chiral moiety.



Mesogenic side group	*n*	*m*	*p*	Mesophase
4a	4	1	1	Cr 39.3 SmC* 48.7 I
4b	4	1	2	Cr 62.8 SmC* 69.0 SmA 118.4 I
4c	4	2	1	Cr 77.4 SmC* 91.9 SmA 141.8 I
4d	4	2	2	Cr 111.6 SmC* 120.9 SmA 260.0 I
4i	9	1	1	Cr 33.5 I
4j	9	1	2	Cr 55.6 SmC* 83.8 SmA 115.5 I
4k	9	2	1	Cr 30.6 SmC* 106.1 SmA 125.9 I
4l	9	2	2	Cr$_1$ 46.6 Cr$_2$ 102.4 SmC* 172.0 SmA 214.7 I

2.2. *Liquid crystalline cyclic siloxane tetramers*

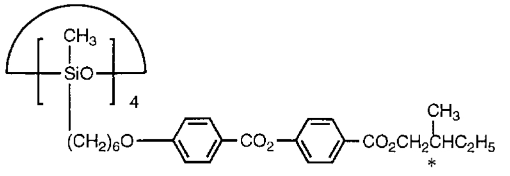
2.2.1. *Explanation of nomenclature*

The following nomenclature has been used for the identification of the cyclic siloxane tetramers prepared in this study. Reference to the mesogenic side group is made at all times to allow ease of cross reference. All cyclic siloxane tetramers are designated as:

$$Cn, yy$$

C = cyclic backbone,
n = number of silicon atoms in the ring, i.e. $n = 4$ for our cyclic tetramers,
yy = the mesogenic side group (see tables 1 and 2 for structure).

The following example shows how the nomenclature system is used.


C4,4e

Structure **2**.

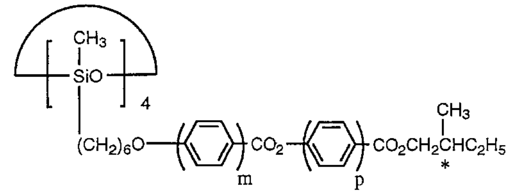
Like the section on the side group precursors, the discussion of results regarding the cyclic siloxane tetramers can also be divided into two sections relating to the structure of the chiral end group.

2.2.2. *Cyclic siloxane tetramers incorporating mesogenic side groups containing the chiral (S)-(−)-2-methylbutyl end group*

The transition temperatures for these cyclic siloxane tetramers are given in tables 3 and 4.

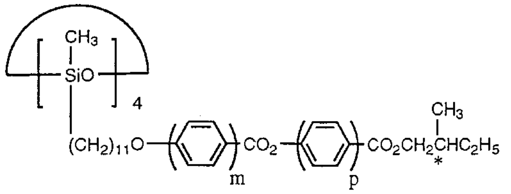
In general, in going from the mesogenic precursor to the cyclic siloxane tetramer we observed an increase in the thermal stabilities of both the SmC* and SmA phases, but the formation of the SmC* was more favoured. For example, the cyclic siloxane tetramers **C4,4h**, **C4,4n** and **C4,4o** did not exhibit a SmA phase. The chiral nematic phase exhibited by compound **4h** and the chiral nematic and Blue Phases of compound **4n** were not shown by their corresponding cyclic siloxane tetramers **C4,4h** and **C4,4n**.

Table 3. The transition temperatures (°C) for the 2MB series cyclic siloxane tetramers containing a $-(CH_2)_6-$ spacer group.



Polymer	Transition temperatures
C4,4e	g − 30.7 SmC* 47.7 I
C4,4f	g 17.9 SmC* 192.4 SmA 201.9 I
C4,4g	g 8.7 SmC* 198.9 SmA 213.0 I
C4,4h	Cr_1 55.3 Cr_2 100.3 SmC* 312.3 I

Table 4. The transition temperatures (°C) for the 2MB series cyclic siloxane tetramers containing a $-(CH_2)_{11}-$ spacer group.



Polymer	Transition temperatures
C4,4m	g − 20.8 SmC* 50.5 I
C4,4n	g 5.5 SmC* 207.8 I
C4,4o	Cr_1 27.3 Cr_2 44.0 SmC* 186.1 I
C4,4p	Cr 97.5 SmC* 275.0 SmA 280.0 I

Cyclic siloxane tetramer **C4,4e** exhibits the behaviour that would be expected for a system that contains a mesogenic side group with only two phenyl rings in the core. The glass transition temperature was sub-ambient (− 30.7°C) and the clearing point was low (47.7°C). This cyclic siloxane tetramer did, however, exhibit a SmC* mesophase whereas the corresponding monomer **4e** was found to exhibit a SmA phase.

For cyclic siloxane tetramer **C4,4f**, there was no change in the mesophases exhibited by the cyclic siloxane tetramer compared with the corresponding monomer. The tetramer exhibited a glass transition to a SmC* phase at 17.9°C and then exhibited a narrow SmA phase (9.5°C) before clearing to the isotropic liquid. The cyclic siloxane tetramer **C4,4g**, which differs from tetramer **C4,4f** only in the arrangement of the phenyl rings in the core of the mesogenic side group, also showed the same mesophase sequence to that exhibited by the cyclic siloxane tetramer **C4,4f**. However, tetramer **C4,4g** showed a slight decrease in the glass transition temperature (9°C), an increase in the SmC* to SmA transition (6°C) and an increase of 11°C in the clearing temperature, compared with cyclic siloxane tetramer **C4,4f**.

As expected, the transition temperatures of the cyclic siloxane tetramer **C4,4h** were very high. This tetramer exhibited only a SmC* phase and had a melting point of 100.3°C. The clearing point for this tetramer was 312.3°C. Again, as in the case of tetramer **C4,4f**, the SmA and N* phases exhibited by the corresponding monomer are not seen in the cyclic siloxane tetramer.

The high temperature of the transitions was due to the presence of two biphenylyl units in the core of the side group. The cyclic siloxane tetramer **C4,4h** exhibited the widest SmC* range of all the 16 tetramers prepared.

In the series of cyclic polysiloxanes **C4,4m–p**, table 4, the mesogenic side group was attached to the cyclic polysiloxane backbone by a spacer unit of eleven carbons in length. The mesogenic side group and chiral end group were kept the same as for cyclic siloxane tetramers **C4,4e–h**, and so it is now possible to study the effect of increase in the spacer length on the thermal properties of the tetramers.

Both cyclic siloxane tetramers **C4,4m** and **C4,4e** exhibited a SmC* phase but in the case of compound **C4,4m**, which had the longer spacer group, this compound exhibited the higher T_g value (by 9.9°) and the higher SmC* to isotropic liquid transition (by 2.8°).

With an increase in the length of the spacer group, the clearing temperature exhibited by the tetramer **C4,4n** showed a slight increase (6°C) over that exhibited by tetramer **C4,4f**. But, unlike cyclic siloxane tetramers **C4,4f** and **C4,4n**, this tetramer showed only a SmC* mesophase. The loss of the SmA, chiral nematic and Blue Phases shown by the precursor of polymer **C4,4n** must be attributed to the incorporation of the mesogenic side groups into the cyclic structure. The glass transition temperature was, however, found to be lower (12°) than that of cyclic siloxane tetramer **C4,4f**.

Cyclic siloxane tetramer **C4,4o** showed a loss of the glass transition to give a crystalline transition at 27°C, compared with the glass transition for tetramer **C4,4g**. Crystallization may be induced by the longer spacer chain. The cyclic siloxane tetramer **C4,4o** exhibited only a smectic C* mesophase, unlike tetramer **C4,4g,** which also showed a SmA phase. The clearing temperature for cyclic siloxane tetramer **C4,4o** was found to be 27°C lower than that of the previously studied tetramer **C4,4g**. It is very clear from the data given in tables 3 and 4 that for tetramers incorporating a mesogenic side group containing three benzene rings, moving to a longer spacer group was not conducive to the formation of the SmA phase.

The thermal transitions shown by the cyclic siloxane tetramer **C4,4p** were again found to be very high. The crystal–SmC* transition temperature for tetramer **C4,4p** was slightly reduced by 3° to 97.5°C compared with tetramer **C4,4h**. The cyclic siloxane tetramer **C4,4p** also exhibited both SmC* and SmA phases, whereas the corresponding tetramer **C4,4h**, which contained the shorter spacer group, exhibited a SmC* phase only. The clearing point for cyclic siloxane tetramer **C4,4p** was reduced by 32° to 280°C compared with that of tetramer **C4,4h**.

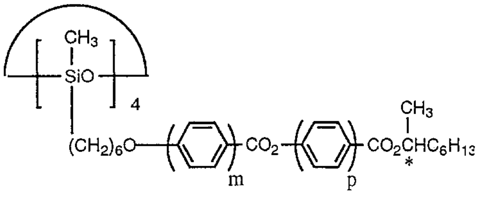
It was interesting to note that out of the eight tetramers synthesized, five exhibited room temperature SmC* phases, and that three out of these five tetramers gave wide SmC* ranges: **C4,4f** (175°), **C4,4g** (190°) and **C4,4n** (202°).

2.2.3. *Cyclic siloxane tetramers incorporating mesogenic side groups containing the chiral (R)-(+)-1-methylheptyl end group*

The transition temperatures for these cyclic siloxane tetramers are given in tables 5 and 6.

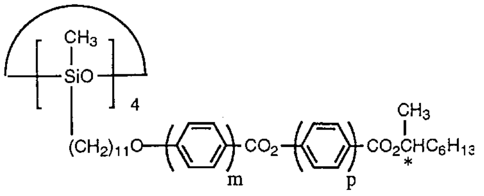
For the cyclic siloxane tetramers with a spacer group containing six carbon atoms, **C4,4a–d**, the formation of the tetramers resulted in an increase in both the SmC* and SmA thermal stabilities, with the emphasis being on the formation of the SmC* phase. This situation was very similar to that found for cyclic siloxane tetramers containing the chiral (*S*)-(−)-2-methylbutyl end group. The only exception was for tetramer **C4,4a**, which did not exhibit liquid crystalline behaviour. For cyclic siloxane tetramers with a spacer group containing eleven carbon atoms, **C4,4i–l**, a decrease in the thermal stabilities for both the SmC* and SmA phases was observed. The only

Table 5. The transition temperatures (°C) for the 2MH series cyclic siloxane tetramers containing a–(CH$_2$)$_6$– spacer group.



Polymer	Transition temperatures
C4,4a	g − 16.7 I
C4,4b	g 16.6 SmC* 117.4 I
C4,4c	g 6.3 SmC* 107.9 SmA 144.5 I
C4,4d	Cr$_1$ 116.3 Cr$_2$ 120.8 SmC* 265.5 I

Table 6. The transition temperatures (°C) for the 2MH series cyclic siloxane tetramers containing a–(CH$_2$)$_{11}$– spacer group.



Polymer	Transition temperatures
C4,4i	Cr − 18.6 SmC* 37.8 I
C4,4j	Cr 25.0 SmC* 71.0 SmA 145.2 I
C4,4k	g 2.1 SmC* 51.3 SmA 143.9 I
C4,4l	Cr$_1$ 67.0 Cr$_2$ 95.8 SmC* 237.2 I

exception to this was found for cyclic siloxane tetramer **C4,4l** where the thermal stability for the SmC* phase increased on polymerization.

Cyclic siloxane tetramers **C4,4a–d** were very similar in structure to tetramers **C4,4e–h**, allowing us to investigate the effect of changing the chiral end group on the phase transitions exhibited by the cyclic siloxane tetramers.

Cyclic siloxane tetramer **C4,4a** exhibited no mesophases and therefore differed from polymer **C4,4e** (the 2-methylbutyl analogue) which exhibited a SmC* phase only.

Cyclic siloxane tetramer **C4,4b** gave a glass transition at 16.6°C and had a clearing temperature of 117.4°C. However, this tetramer did not show the usual SmC* and SmA phases exhibited by all the other cyclic siloxane tetramers containing three phenyl rings and a six carbon unit spacer group. Cyclic siloxane tetramer **C4,4c** showed a decrease in the glass transition temperature (10°C) compared with tetramer **C4,4b** and was found to exhibit both SmC* and SmA phases. As found for the tetramers in the 2MB series with a spacer group length of 6, the clearing temperature of tetramer **C4,4c** was higher (27°C) than that found for tetramer **C4,4b**.

For the cyclic siloxane tetramer **C4,4d** the transition temperatures were again very high. The Cr–SmC* transition temperature was 120.8°C and the clearing temperature was 265.5°C. The clearing temperature was found to be 47°C lower than that for tetramer **C4,4h**, the 2-methylbutyl analogue. The Cr–SmC* transition temperature for tetramer **C4,4d** was, however, found to be higher by 21°C than that for tetramer **C4,4h**.

In the case of tetramer **C4,4i–l** the spacer group was again lengthened to eleven carbon units in length. The introduction of a longer spacer group allowed the formation of a SmC* mesophase for the cyclic siloxane tetramer **C4,4i**. This was in contrast to tetramer **C4,4a** which exhibited no mesophase. The increase in mass of the mesogenic side group along with a stronger decoupling of the motions of the side group from the constraints imposed by the cyclic tetramer backbone may have contributed to the formation of a mesophase for tetramer **C4,4i**.

Cyclic siloxane tetramer **C4,4j** showed a loss of the glass transition temperature and exhibited a crystalline melting temperature of 25°C, compared with the glass transition of 2.1°C found for tetramer **C4,4k**. The other surprising feature about these two cyclic siloxane tetramers was the low thermal stability for the SmC* phase. The average smectic C* stability for polymers **C4,4j** and **C4,4k** was about half that found for the analogous tetramers incorporating a six carbon spacer group and about 30% of that found for cyclic siloxane tetramers containing the chiral 2-methylbutyl end group. Indeed, this series of cyclic siloxane tetramers gave the lowest thermal stability for the SmC* of all the cyclic siloxane tetramers studied. The changing of the chiral end group from 2-methylbutyl to 1-methylheptyl, coupled to lengthening of the spacer group from six to eleven carbon atoms, is not conducive to the formation of a SmC* phase.

The cyclic siloxane tetramer that contained a four ring mesogenic side group **C4,4l** again exihibted very high transition temperatures. The melting point was 95.7°C and the clearing temperature for the SmC* phase was 237.2°C. This was lower (28°C) than the clearing temperature for tetramer **C4,4d** which had a shorter spacer group.

3. Summary

A detailed summary of the effects of (a) the length of the spacer group, (b) the arrangement of the phenyl rings in the mesogenic side group core and (c) the structure of the chiral end group, on the thermal properties of the cyclic siloxane tetamers are now given (cf. structure 1).

(1) The effect of the number and arrangement of phenyl rings in the mesogenic side group core on:

(a) *SmC* thermal stability*

X	*n*	Ratio *a*:*b*
$CH_2CH(CH_3)C_2H_5$	6	2:2 > 2:1 > 1:2 > 1:1
$CH_2CH(CH_3)C_2H_5$	11	2:2 > 1:2 > 2:1 > 1:1
$CH(CH_3)CH_2C_5H_{11}$	6	2:2 > 1:2 > 2:1 > 1:1
$CH(CH_3)CH_2C_5H_{11}$	11	2:2 > 1:2 > 2:1 > 1:1

(b) *Glass transition temperatures/crystalline transition temperatures*

X	*n*	Ratio *a*:*b*
$CH_2CH(CH_3)C_2H_5$	6	2:2 ≫ 1:2 > 2:1 ≫ 1:1
$CH_2CH(CH_3)C_2H_5$	11	2:2 ≫ 2:1 > 1:2 ≫ 1:1
$CH(CH_3)CH_2C_5H_{11}$	6	2:2 ≫ 1:2 > 2:1 ≫ 1:1
$CH(CH_3)CH_2C_5H_{11}$	11	2:2 ≫ 1:2 > 2:1 ≫ 1:1

All the glass transition temperatures for the cyclic siloxane tetramers where the ratio of the phenyl rings (*a*:*b*) was 1:1 were below − 15°C.

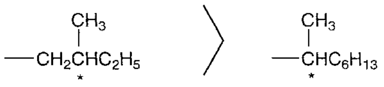
(c) *SmC* ranges*

X	*n*	Ratio *a*:*b*
$CH_2CH(CH_3)C_2H_5$	6	2:2 > 2:1 > 1:2 ≫ 1:1
$CH_2CH(CH_3)C_2H_5$	11	1:2 > 2:2 > 2:1 ≫ 1:1
$CH(CH_3)CH_2C_5H_{11}$	6	2:2 > 2:1 > 1:2
$CH(CH_3)CH_2C_5H_{11}$	11	2:2 > 1:1 > 2:1 > 1:2

Ten out of the 16 cyclic siloxane tetramers gave room temperature SmC* phases and some of these also gave very wide SmC* ranges. A selection of these tetramers is given below.

C4,4n	SmC* range = 202.3°C (T_g 5.5°C)
C4,4g	SmC* range = 190.2°C (T_g 8.7°C)
C4,4c	SmC* range = 101.6°C (T_g 6.3°C)

(2) The effect of the structure of the chiral end group on (a) SmC* thermal stability, (b) glass transition temperatures/crystalline transition temperatures, and (c) SmC* ranges, for all the cyclic siloxane tetramers, always varied in the order:



$—CH_2\underset{*}{\overset{CH_3}{C}}HC_2H_5 > —\underset{*}{\overset{CH_3}{C}}HC_6H_{13}$

2MB **2MH**

(3) For a given chiral end group, the effect of the length of the spacer group on (a) SmC* thermal stability, (b) glass transition temperatures/crystalline transition temperatures and (c) SmC* ranges, depended greatly on the arrangement of the phenyl rings in the mesogenic side group.

(a) *SmC* thermal stability*
For polymers containing the 2MB chiral end group:
Spacer group $n = 6 > n = 11$, for polymers where ratio of $a{:}b = 2{:}1$ and $2{:}2$.
Spacer group $n = 11 > n = 6$, for polymers where ratio of $a{:}b = 1{:}1$ and $1{:}2$.
For all polymers containing the 2MH chiral group:
Spacer group $n = 6 > n = 11$.

(b) *Glass transition temperatures/crystalline transition temperatures*
For polymers containing the 2MB chiral group:
Spacer group $n = 6 > n = 11$, for polymers where ratio of $a{:}b = 1{:}2$ and $2{:}2$.
Spacer group $n = 11 > n = 6$, for polymers where ratio of $a{:}b = 1{:}1$ and $2{:}1$.
For all polymers containing the 2MH chiral group:
Spacer group $n = 6 > n = 11$, for polymers where the ratio $a{:}b = 1{:}1$, $2{:}1$ and $2{:}2$.
Spacer group $n = 11 > n = 6$, for polymers where the ratio $a{:}b = 1{:}2$.

(c) *SmC* ranges*
For polymers containing the 2MB chiral group:
Spacer group $n = 6 > n = 11$, for polymers where ratio of $a{:}b = 1{:}1$, $2{:}1$ and $2{:}2$.
Spacer group $n = 11 > n = 6$, for polymers where ratio of $a{:}b = 1{:}2$.
For all polymers containing the 2MH chiral group:
Spacer group $n = 6 > n = 11$, for polymers where the ratio $a{:}b = 1{:}2$, $2{:}1$ and $2{:}2$.
Spacer group $n = 11 > n = 6$, for polymers where the ratio $a{:}b = 1{:}1$ (polymer **C4,4a** where $n = 6$ did not exhibit LC behaviour).

4. Conclusions

All the cyclic siloxane tetramers, except tetramer **C4,4a**, exhibited a SmC* phase with six out of the sixteen cyclic siloxane tetramers also exhibiting a SmA phase. Ten out of the sixteen cyclic siloxane tetramers gave glass/crystalline transition temperatures below room temperature. For the two series of cyclic siloxane tetramers studied it is possible to identify trends in their liquid crystalline behaviour.

(1) Increasing the length of the spacer group or having two biphenylyl units in the mesogenic side group generally meant that the cyclic siloxane tetramer exhibited a crystalline instead of a glass transition temperature.
(2) The effect of changing the chiral end group from 2-methylbutyl to 1-methylheptyl on the thermal properties of the tetramers generally resulted in an overall reduction in (a) the thermal stability of the mesophases, (b) the glass or crystalline transition temperatures and (c) SmC* ranges exhibited.
(3) The effect of the arrangement of the phenyl rings in the mesogenic core on the SmC* and glass transition/crystalline transition temperatures generally followed the order
Ratio $a{:}b$ $2{:}2 > 1{:}2 > 2{:}1 > 1{:}1$
(see structure 1).
(4) However, the effect of the arrangement of the phenyl rings on the SmC* ranges exhibited by the cyclic siloxane tetramers was varied, and depended on both the length of the spacer group and the structure of the chiral end group.
(5) For a given chiral end group the effect of the length of the spacer group on, (a) SmC* thermal stability, (b) glass transition temperatures/crystalline transition temperatures and (c) SmC* ranges, depended greatly on the arrangement of the phenyl rings in the mesogenic side group. In general, however, increasing the length of the spacer group gave cyclic siloxane tetramers with higher SmC* thermal stabilities, glass/crystalline transition temperatures and SmC* ranges.
(6) This work has produced a variety of SGLC polymers exhibiting wide room temperature SmC* (ferroelectric) ranges. A selection of these is given below.

Polymer **C4,4e**	T_g − 30.7 SmC* 47.7°C I
Polymer **C4,4m**	T_g − 20.8 SmC* 50.5°C I
Polymer **C4,4b**	T_g 16.6 SmC* 117.4°C I
Polymer **C4,4n**	T_g 5.5 SmC* 207.8°C I

5. Experimental

The synthetic routes to the monomers and cyclic siloxane tetramers are given in schemes 1 and 2.

5.1. *Characterization*

^{1}H NMR spectra were obtained using a JMN GX270FT spectrometer, with deuteriated chloroform as solvent and tetramethylsilane as the internal standard. The peak types in the spectra are denoted by the following notations: singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Infrared spectra were obtained using a Perkin Elmer 487G or a Perkin Elmer 983G spectrophotometer. Samples were prepared as either potassium bromide discs or, if liquid, on single crystal sodium chloride discs. Mass spectra were obtained using a Finnigan 1020 GCMS spectrometer. Results are quoted where M^+ represents the molecular ion and the base peak represented by (100%).

Optical rotational measurements were obtained using a ETL-NPL automatic polarimeter control unit Type 143A. The sample was prepared as 0.1 g of sample in 1 cm^3 of chloroform. Results are quoted at ambient temperature using a monochromatic sodium light source. Differential scanning calorimetry (DSC) thermograms were obtained using a Perkin Elmer DSC 7, with a TAC 7/PC interface and a controlled cooling accessory. Heating rate was initially 20°C min^{-1} and then 10°C min^{-1}. Calculations were made using Perkin Elmer UNIX based software. Optical microscopy was performed using an Olympus BH2 polarizing microscope fitted with a Mettler FP52 hot stage and a Mettler FP5 controller. Samples were prepared as thin films between a glass slide and a glass cover slip.

Column chromatography was carried out under flash chromatography conditions, unless stated otherwise. The stationary phase used was Sorbsil C60 (40–60 µm). Thin layer chromatography (TLC) was performed on aluminium sheets coated in Merck Kieselgel silica gel 60 F_{254}, eluting with dichloromethane. In the case of the carboxylic acids, ethyl acetate was used as the mobile phase. All the compounds from schemes 1 and 2 gave a single spot.

Analytical high performance liquid chromatography (HPLC) measurements were made on a reversed phase HPLC column (5 µm, 25 × 0.46 cm, Dynamax Microsorb C18 column) in conjunction with a Spectroflow 757 UV detector (254 nm) with data handling software. The mobile phase was acetonitrile. For compounds **4a–p** in scheme 2, the purity of the compounds was $>99.5\%$. Gel permeation chromatography (GPC) measurements were carried out using a Gilson refractive index detector model 131, a Kontron HPLC pump model 420 and PLgel column (5 µm, 30 × 0.75 cm mixed-C column). The column was calibrated by using a series of polystyrene standards. Toluene was used as the internal standard with tetrahydrofuran (THF) as the mobile phase.

5.2. *Preparation of materials*

The synthetic route to the monomers is given in scheme 1.

5.2.1. *4-(Methoxycarbonyloxy)benzoic acid*

4-Hydroxybenzoic acid (20.0 g, 0.15 mol) was added, with stirring, to a solution of sodium hydroxide (16.8 g, 0.42 mol) in water (1000 ml) at 0°C. Methyl chloroformate (22.4 g, 0.24 mol) was added slowly to the suspension and the temperature maintained at 0°C. The mixture was stirred for 4 h at room temperature and then brought to pH 4–5 by the addition of a mixture of concentrated hydrochloric acid and water (1 : 1). The voluminous white precipitate was filtered off and recrystallized (ethanol) to yield 4-(methoxycarbonyloxy)-benzoic acid as a white powder. Yield 20.4 g (70%), m.p. 178–179°C. ^{1}H NMR ($CDCl_3$) δ 8.15 (2H, d), 7.30 (2H, d), 3.95 (3H, s). IR (KBr) ν_{max} 3700–3300, 2800, 1760, 1690 cm^{-1}. MS *m/z* 196 (M^+), 152 (100%), 135, 59.

5.2.2. *(S)-(−)-2-Methylbutyl 4-(methoxycarbonyloxy)-benzoate*

A solution of triphenylphosphine (10.5 g, 0.04 mol) in dry THF (50 ml) was added over 1 min to a stirred solution of 4-(methoxycarbonyloxy)benzoic acid (7.8 g, 0.04 mol), (*S*)-(−)-2-methyl-1-butanol (3.53 g, 0.04 mol) and diethyldiazodicarboxylate (6.97 g, 0.04 mol) in dry THF (100 ml), under an atmosphere of dry nitrogen. The solution was stirred overnight at room temperature and the solvent removed by distillation under reduced pressure. The crude ester was purified by flash column chromatography (silica gel, dichloromethane) to yield (*S*)-(−)-2-methylbutyl 4-(methoxycarbonyloxy)benzoate as a colourless oil. Yield 10.3 g (98%). ^{1}H NMR ($CDCl_3$)δ 8.10 (2H, d), 7.25 (2H, d), 4.20 (2H, m), 3.90 (3H, s), 1.85 (1H, m), 1.55 (2H, m), 1.30 (2H, m), 1.00 (6H, m). IR (KBr) ν_{max} 2950, 2890, 1770, 1720, 1610, 1450, 1260 cm^{-1}. MS *m/z* 267(M^+), 179, 152, 70 (100%). $[\alpha]_D = -9.8°$.

(R)-(+)-1-Methylheptyl 4-(methoxycarbonyloxy)-benzoate was prepared using a similar procedure to that outlined for the preparation of (*S*)-(−)-2-methylbutyl 4-(methoxycarbonyloxy)benzoate. The crude ester was purified by column chromatography (silica gel, dichloromethane) to yield (*R*)-(+)-1-methylheptyl 4-(methoxycarbonyloxy)benzoate as a pale yellow oil. Yield 2.2 g (58%). ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d), 7.30 (2H, d), 5.20 (1H, m), 3.90 (3H, s), 1.5 (13H, m), 0.85 (3H, m). IR (KBr) ν_{max} 2950, 2880, 1770, 1710, 1600, 1440, 1250, 1100 cm^{-1}. MS *m/z* 308 (M^+), 197 (100%), 179, 152, 135. $[\alpha]_D = +28.8°$.

5.2.3. *(S)-(−)-2-Methylbutyl 4-hydroxybenzoate*

(*S*)-(−)-2-Methylbutyl 4-(methoxycarbonyloxy)-benzoate (10.26 g, 0.036 mol) was added to a mixture of ethanol (75 ml) and ammonia (25 ml) and stirred for 4 h at room temperature. The solvent was removed by distillation under reduced pressure. Ether (100 ml) was added to the residue and the etheral solution washed with saturated sodium hydrogen carbonate (3 × 50 ml), water (2 × 50 ml) and dried ($MgSO_4$). The ether was then removed by distillation under reduced pressure to yield (*S*)-(−)-2-methylbutyl 4-hydroxybenzoate as a pale yellow viscous oil. Yield 7.2 g (95%). ^{1}H NMR ($CDCl_3$) δ 8.00 (3H, d), 6.90 (2H, d), 4.15 (2H, m), 2.20 (2H, s), 1.80 (1H, m), 1.50 (1H, m), 1.25 (1H, m), 1.00 (6H, m). IR (KBr) ν_{max} 3350, 2980, 2960, 1710, 1680, 1610, 1590 cm^{-1}. MS *m*/*z* 208 (M^+), 139, 121 (100%), 93, 70. $[\alpha]_D = -6.8°$.

(R)-(+)-1-Methylheptyl 4-hydroxybenzoate was prepared using a similar procedure. Yield 4.7 g (98%) ^{1}H NMR ($CDCl_3$) δ 7.95 (2H, d), 7.10 (1H, s), 6.85 (2H, d), 5.10 (1H, m), 3.50 (2H, m), 1.70 (3H, m), 1.30 (15H, m), 0.85 (3H, m). IR (KBr) ν_{max} 3300, 3000, 2970, 1700, 1680, 1600, 1590 cm^{-1}. MS *m*/*z* 250 (M^+), 138 (100%), 121, 69, 55. $[\alpha]_D = +28.8°$.

5.2.4. *Esters of 4′-hydroxybiphenyl-4-carboxylic acid*

4′-Hydroxybiphenyl-4-carboxylic acid was prepared by a standard method from 4′-hydroxy-4-cyanobiphenyl, and esterified to give (*S*)-(−)-2-methylbutyl 4′-hydroxybiphenyl-4-carboxylate using a similar procedure to that for the preparation of (*S*)-(−)-2-methylbutyl 4-(methoxycarbonyloxy)benzoate. The crude ester was purified by flash column chromatography (silica gel, dichloromethane) to yield (*S*)-(−)-2-methylbutyl 4′-hydroxybiphenyl-4-carboxylate as a white solid. Yield 4.0 g (58%), m.p. 115–116°C. ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, m), 7.55 (4H, m), 6.95 (2H, m), 5.45 (1H, s), 4.20 (2H, m), 1.85 (1H, m), 1.55 (1H, m), 1.35 (1H, m), 1.0 (6H, m). IR (KBr) ν_{max} 3400, 2940, 2920, 2890, 1680, 1600, 1590 cm^{-1}. MS *m*/*z* 343 (M^+), 255, 228, 70 (100%). $[\alpha]_D = -2.9°$.

(R)-(+)-1-Methylheptyl 4′-hydroxybiphenyl-4-carboxylate was prepared similarly. The crude ester was purified by flash column chromatography (silica gel, dichloromethane) to yield (*R*)-(+)-(1-methylheptyl)-4′-hydroxybiphenyl-4-carboxylate as a white crystalline solid. Yield 2.2 g (56%), m.p. 76–77°C. ^{1}H NMR ($CDCl_3$) δ 8.10 (1H, d), 7.60 (2H, q), 6.95 (1H, d), 5.20 (1H, m), 1.50 (11H, m), 0.95 (3H, m). IR (KBr) ν_{max} 3360, 2980, 2920, 2860, 1680, 1600, 1590, 1300, 1270 cm^{-1}. $[\alpha]_D = +42.2°$.

5.2.5. *4-(Hex-5-enyloxy)benzoic acid*

A solution of 4-hydroxybenzoic acid (9.01 g, 0.065 mol) in ethanol (40 ml) was added to a solution of sodium hydroxide (5.6 g, 0.14 mol) in water (20 ml). The reaction mixture was heated to boiling and 6-bromo-1-hexene (11.74 g, 0.072 mol) was added dropwise to the solution and the resulting reaction mixture was then heated under reflux for 21 h. The excess ethanol was removed by distillation under reduced pressure and the residue diluted with water (40 ml). The cooled reaction mixture was acidified with concentrated hydrochloric acid (10 ml) and the crude product filtered off, washed with water and recrystallized (50% aqueous ethanol) to yield 4-(hex-5-enyloxy)benzoic acid as a white crystalline solid. Yield 11.4 g (95%), Cr 101 N 140 C I (°C). ^{1}H NMR ($CDCl_3$) δ 8.10 (2H, d), 6.95 (2H, d), 5.85 (1H, m), 5.05 (2H, t), 4.05 (2H, t), 2.15 (2H, m), 1.85 (2H, m), 1.60 (2H, m). IR (KBr) ν_{max} 2950, 1690, 1610, 1260 cm^{-1}. MS *m*/*z* 220 (M^+), 203, 138, 82, 55 (100%).

5.2.6. *Ethyl 4-(undec-10-enyloxy)benzoate*

Ethyl 4-(undec-10-enyloxy)benzoate was prepared using a similar procedure to that for the preparation of (*S*)-(−)-2-methylbutyl 4-(methoxycarbonyloxy)benzoate. The crude product was purified by column chromatography (silica gel, dichloromethane to yield ethyl 4-(undec-10-enyloxy)benzoate as a yellow oil. Yield 18.1 g (97%). ^{1}H NMR ($CDCl_3$) δ 8.00 (2H, q), 6.90 (2H, q), 5.80 (1H, m), 4.90 (2H, t), 3.65 (2H, t), 3.40 (2H, q), 2.00 (2H, m), 1.60–1.30 (17H, m). IR (KBr) ν_{max} 3000–2850, 1720, 1600, 1500, 1270, 1250, 1170 cm^{-1}. MS *m*/*z* 318 (M^+), 289, 165, 153 (100%), 125.

5.2.7. *4-(Undec-10-enyloxy)benzoic acid*

A solution of sodium hydroxide (10.00 g, 0.25 mol) in water (100 ml) was added to a stirred solution of ethyl 4-(undec-10-enyloxy)benzoate (10.00 g, 0.03 mol) in ethanol (50 ml) and the resulting reaction mixture was then heated under reflux for 4 h. The solution was allowed to cool to room temperature and water (250 ml) was added. The solution was then brought to pH 7 (universal indicator paper) by the addition of concentrated hydrochloric acid. The resulting precipitated acid was filtered off and recrystallized (ethanol) to yield 4-(undec-10-enyloxy)benzoic acid as a white solid. Yield 6.6 g (75%), Cr 79 SmC 106 N 138 I (°C). ^{1}H NMR ($CDCl_3$) δ 8.05 (2H, d), 6.90 (2H, d), 5.80 (1H, m), 4.95 (2H, t), 3.45 (2H, t), 2.10 (2H, m), 1.80 (2H, m), 1.50–1.25 (12H, m). IR(KBr) ν_{max} 3500–2500, 3100–2800, 1680, 1600, 1500, 1450, 1250, 1160 cm^{-1}. MS *m*/*z* 289 (M^+), 272, 153, 136 (100%), 126.

5.2.8. *Methyl 4′-hydroxybiphenyl-4-carboxylate*

To a stirred solution of 4′-hydroxybiphenyl-4-carboxylic acid (6.70 g, 0.0073 mol) in methanol (100 ml) was added concentrated sulphuric acid (2 drops) and the solution was then heated under reflux, with stirring, overnight. The solvent was removed by distillation under reduced pressure and the product purified by recrystallization (ethanol) to yield methyl 4′-hydroxybiphenyl-4-carboxylate as a white crystalline solid. Yield 8.6 g (99%), m.p. 85–86°C. ^{1}H NMR ($CDCl_3$) δ 8.30 (1H, s), 8.05 (2H, d), 7.60 (2H, d), 7.50

(2H, d), 6.95 (2H, d), 3.95 (3H, s). IR (KBr) ν_{max} 3400, 2960, 1680, 1600, 1590, 1300 cm^{-1}. MS *m/z* 228 (M^+), 197, 181, 115, 90, 84, 81, 64, 58 (100%).

5.2.9. *Methyl 4′-(hex-5-enyloxy)biphenyl-4-carboxylate*

Methyl 4′-hydroxybiphenyl-4-carboxylate (7.14 g, 0.03 mol), 6-bromo-1-hexene (5.10 g, 0.031 mol), potassium carbonate (20 g, 0.12 mol), potassium iodide (0.1 g) in dry butanone (100 ml) were heated under reflux, with stirring, overnight. The potassium salts were removed by filtration and the solvent removed by distillation under reduced pressure. The crude ester was then purified by column chromatography (silica gel, dichloromethane), followed by recrystallization (ethanol) to yield methyl 4′-(hex-5-enyloxy)biphenyl-4-carboxylate as a white crystalline solid. Yield 8.8 g (92%), m.p. 56–57°C. ^1H NMR ($CDCl_3$) δ 8.10 (2H, d), 7.55 (4H, m), 6.95 (2H, d), 5.85 (1H, m), 5.05 (2H, m), 4.05 (2H, t), 3.95 (3H, s), 2.15 (2H, m), 1.80 (2H, m), 1.60 (2H, m). IR (KBr) ν_{max} 2990, 2920, 2880, 1740, 1600, 1300 cm^{-1}. MS *m/z* 311 (M^+), 305, 296, 292, 227, 138, 82, 55 (100%).

5.2.10. *4′-(Hex-5-enyloxy)biphenyl-4-carboxylic acid (**3c**, scheme 1)*

This was prepared using a similar procedure to that for the preparation of 4-(undec-10-enyloxy)benzoic acid. Recrystallization (ethanol) yielded 4′-(hex-5-enyloxy)-biphenyl-4-carboxylic acid (**3c**) as a white solid. Yield 7.4 g (83%). Cr 201 SmC 231 N 264 I (°C). ^1H NMR ($CDCl_3$) δ 8.10 (2H, d), 7.60 (4H, m), 7.00 (2H, d), 5.85 (1H, m), 5.00 (2H, m), 4.05 (2H, t), 2.15 (2H, m), 1.80 (2H, m), 1.65 (2H, m). IR (KBr) ν_{max} 3100–2900, 2940, 2700, 1680, 1600, 1590 cm^{-1}. MS *m/z* 296 (M^+), 279, 214, 138, 82, 55 (100%).

5.2.11. *Methyl 4′-(undec-10-enyloxy)biphenyl-4-carboxylate*

This was prepared using a similar procedure to that for (*S*)-(−)-2-methylbutyl 4-(methoxycarbonyloxy)-benzoate. The crude product was purified by column chromatography (silica gel, dichloromethane) to yield methyl 4′-(undec-10-enyloxy)biphenyl-4-carboxylate as a white crystalline solid. Yield 3.5 g (97%), m.p. 165–167°C. ^1H NMR ($CDCl_3$) δ 8.08 (2H, d), 6.65 (2H, d), 7.58 (2H, d), 6.98 (2H, d), 5.80 (2H, m), 4.95 (1H, m), 4.00 (2H, t), 3.93 (3H, s), 2.08 (2H, m), 1.85 (2H, m), 1.50–1.25 (12H, m). IR (KBr) ν_{max} 3000–2820, 1720, 1600, 1440, 1280, 1200, 1110, 840 cm^{-1}. MS *m/z* 380 (M^+), 349, 338, 228, 211, 197, 168, 151, 139, 115, 83, 69, 55.

The preparation of *4′-(undec-10-enyloxy)biphenyl-4-carboxylic acid (**3d**, scheme 1)* was similar to that for the preparation of 4′-(hex-5-enyloxy)biphenyl-4-carboxylic acid (**3c**). The resulting precipitated acid was recrystallized (ethanol) to yield 4′-(undec-10-enyloxy)biphenyl-4-carboxylic acid (**3d**) as a white crystalline solid. Yield 3.2 g (98%), Cr 160 N 246 I (°C). ^1H NMR ($CDCl_3$) δ 8.05–8.15 (2H, d), 7.5–7.65 (4H, q), 6.95–7.05 (2H, d), 5.75–5.9 (1H, m), 4.9–5.05 (2H, m), 3.95–4.04 (2H, t), 1.95–2.1 (2H, m), 1.75–1.85 (2H, m), 1.2–1.5 (12H, m). IR (KBr) ν_{max} 3040, 2500–3000, 1680, 1600, 1525, 1430, 1250, 990, 910, 830 cm^{-1}. MS *m/z* 366 (M^+), 214 (100%), 197, 152, 139, 115, 83, 69.

5.2.12. *(S)-(−)-2-Methylbutyl 4-[4′-(hex-5-enyloxy)-biphenyl-4-carbonyloxy]benzoate (**4g**)*

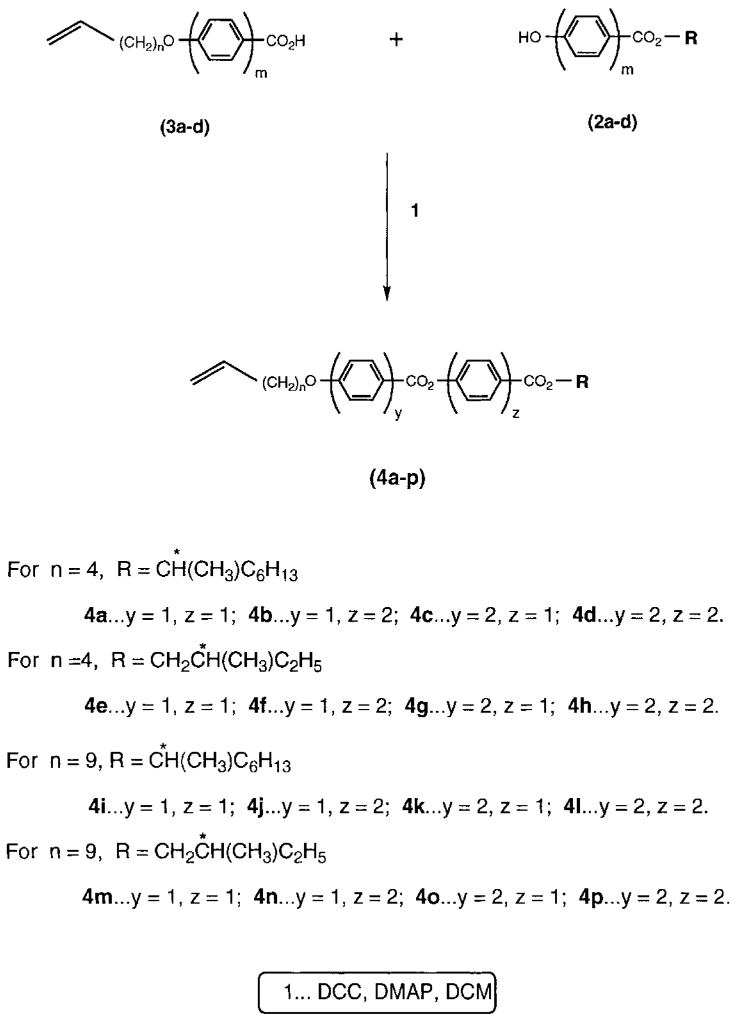
The preparation compound **4g** exemplifies the procedure used to prepare compounds **4a–p**, see scheme 2.

4′-(Hex-5-enyloxy)biphenyl-4-carboxylic acid (**3c**) (2.30 g, 8.21 mmol), (*S*)-(−)-2-methylbutyl-4′-hydroxy-benzoate (1.55 g, 7.50 mmol) and dimethylaminopyridine (0.09 g, 7.5 mmol) were dissolved in dry dichloromethane (60 ml) under anhydrous conditions. *N*,*N*-Dicyclohexyl-carbodiimide (1.55 g, 7.50 mmol) in dry dichloromethane (15 ml) was added and the reaction mixture allowed to stir, at room temperature, overnight. The prepicitated DCU was filtered off and the solvent removed by distillation under reduced pressure. The crude ester was then purified by flash column chromatography (silica gel, dichloromethane) and recrystallization (acetonitrile) to yield (*S*)-(−)-2-methylbutyl 4-[4′-(hex-5-enyloxy)biphenyl-4-carbonyloxy]benzoate (**4g**) as a white crystalline solid. Yield 1.0 g (30%), Cr 85.6 SmC* 107.8 SmA 189.7 I (°C). ^1H NMR ($CDCl_3$) δ 8.20 (4H, m), 7.65 (4H, m), 7.35 (2H, m), 7.10 (2H, m), 5.85 (2H, m), 5.05 (1H, m), 4.20 (2H, m), 4.10 (2H, t), 2.15 (2H, m), 1.85 (3H, m), 1.60 (2H, m), 1.35 (1H, m), 1.00 (6H, m). IR (KBr) ν_{max} 2980–2920, 1720, 1600, 1290 cm^{-1}. MS *m/z* 486 (M^+), 399, 279 (100%). $[\alpha]_D = -18.7°$.

Compounds **4a–f** and **4h–p** (scheme 1) were prepared using a similar procedure to that for compound **4g**. Compounds **4e** and **4f** have been previously synthesized by Mrs J. Haley (University of Hull).

*(R)-(+)-1-Methylheptyl 4-[4′-(hex-5-enyloxy)phenyl-1-carbonyloxy]benzoate (**4a**).* Yield 2.9 g (70%), Cr 39.3 SmC* 48.7 I (°C). ^1H NMR ($CDCl_3$) δ 8.15 (4H, q), 7.25 (2H, q), 6.95 (2H, q), 5.85 (2H, m), 5.10 (1H, m), 4.00 (2H, m), 2.15 (2H, m) 1.60 (15H, m), 0.90 (3H, m). IR (KBr) ν_{max} 2980, 2970, 1730, 1710, 1600, 1510 cm^{-1}. MS *m/z* 452 (M^+), 312, 109, 91 (100%), 71, 65, 55. $[\alpha]_D = +27.2°$

*(R)-(+)-1-Methylheptyl 4-[4′-(hex-5-enyloxy)phenyl-1-carbonyloxy]biphenyl-4-carboxylate (**4b**).* Yield 1.8 g (55%), Cr 62.8 SmC* 69.0 SmA 118.4 I (°C). ^1H NMR ($CDCl_3$) δ 8.15 (4H, m), 7.65 (4H, m), 7.30 (2H, m), 6.95



Scheme 1.

(2H, d), 5.85 (2H, m), 5.15 (1H, m), 4.05 (2H, m), 2.15 (2H, m), 1.25 (17H, m), 0.85 (4H, m). IR (KBr) ν_{max} 2900, 2870, 1710, 1700, 1600, 1270 cm^{-1}. MS *m/z* 528 (M$^+$), 453, 341, 323, 214, 203 (100%), 197, 169, 139, 121, 115, 65, 55, 45. $[\alpha]_D = +12.7°$.

*(R)-(+)-1-Methylheptyl 4-[4'-(hex-5-enyloxy)biphenyl-4-carbonyloxy]benzoate (**4c**).* Yield 1.8 g (45%), Cr 77.4 SmC* 91.9 SmA 141.8 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.20 (4H, m), 7.65 (4H, m), 7.30 (2H, d), 7.00 (2H, m), 5.85 (2H, m), 5.00 (1H, m), 4.05 (2H, t), 1.85 (11H, m), 1.35 (13H, m), 0.85 (3H, m). IR (KBr) ν_{max} 2940, 2860, 1760, 1720, 1600, 1280 cm^{-1}. MS *m/z* 528 (M$^+$), 399, 369, 355, 279 (100%), 197, 141, 105, 69, 55, 45. $[\alpha]_D = +19.1°$.

*(R)-(+)-1-Methylheptyl 4-[4'-(hex-5-enyloxy)biphenyl-4-carbonyloxy]biphenyl-4-benzoate (**4d**).* Yield 1.1 g (45%), Cr 111.6 SmC* 120.9 SmA 260.0 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.20 (4H, m), 7.65 (8H, m), 7.35 (2H, d), 7.00 (2H, d), 5.85 (2H, m), 5.15 (1H, m), 5.05 (2H, m), 4.05 (2H, t), 2.15 (2H, m), 1.65 (17H, m), 0.85 (3H, m). IR (KBr) ν_{max} 2940, 2880, 1740, 1720, 1620, 1600, 1310, 1280, 1200 cm^{-1}. MS *m/z* 604 (M$^+$),486, 468, 423, 312, 279 (100%), 55. $[\alpha]_D = +19.2°$.

*(S)-(−)-2-Methylbutyl 4-[4'-(hex-5-enyloxy)biphenyl-4-carbonyloxy]biphenyl-4-carboxylate (**4h**).* Yield 1.9 g (70%), Cr$_1$ 105.1 Cr$_2$ 113.3 SmC* 181.6 SmA 292.6 N* 307.7 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.25 (2H, d), 8.15 (2H, d), 7.65 (8H, m), 7.35 (2H, d), 7.00 (2H, d), 5.85 (2H, m), 5.00 (1H, t), 4.20 (2H, m), 4.05 (2H, t), 2.20 (2H, m), 1.60 (4H, m), 1.60 (3H, m), 1.30 (1H, m), 1.00 (6H, m). IR (KBr) ν_{max} 2940, 2920, 2880, 1720, 1600, 1260 cm^{-1}. MS *m/z* 562 (M$^+$), 494, 475, 392, 279 (100%), 211, 197, 168, 152, 141, 55, 45. $[\alpha]_D = -2.2°$.

*(R)-(+)-1-Methylheptyl 4-[4'-(undec-10-enyloxy)-phenyl-1-carbonyloxy]benzoate (**4i**).* The crude ester was purified by flash column chromatography (dichloromethane, silica gel) and recrystallization (ethanol) to yield **4i** as a white crystalline solid. Yield 0.80 g (38%), Cr 33.5 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.14 (2H, d), 8.11

(2H, d), 7.28 (2H, d), 6.98 (2H, d), 5.80 (2H, m), 5.15 (1H, m), 4.95 (2H, t), 4.05 (2H, t), 2.10 (2H, m), 1.80-1.20 (27H, m), 0.85 (3H, t). IR (KBr) $\nu_{\max}$ 3000–2825, 1720, 1710, 1600, 1510, 1260, 1200, 1160 cm^{-1}. MS *m/z* 523 (M^{+}), 411, 393, 273 (100%), 231, 147, 133, 121, 107, 93, 65, 55, 45. $[\alpha]_{\mathrm{D}} = +8.6^{\circ}$.

(R)-(+)-1-Methylheptyl 4-[4'-(undec-10-enyloxy)phenyl-1-carbonyloxy]biphenyl-4-carboxylate (**4j**). Yield 1.0 g (65%), Cr 55.6 SmC* 83.8 SmA 115.5 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.17 (2H, d), 8.11 (2H, d), 7.67 (2H, d), 7.64 (2H, d), 7.31 (2H, d), 6.98 (2H, d), 5.80 (2H, m), 5.15 (1H, m), 4.95 (2H, t), 4.00 (2H, t), 2.05 (2H, m), 1.80 (2H, m), 1.60–1.20 (25H, m), 0.90 (3H, t). IR (KBr) $\nu_{\max}$ 3100–2825, 1730, 1710, 1600, 1520, 1260, 1210, 1160 cm^{-1}. MS *m/z* 600 (M^{+}), 470, 349, 316, 233 (100%), 231, 213, 196, 121, 65, 55. $[\alpha]_{\mathrm{D}} = +28.0^{\circ}$.

(R)-(+)-1-Methylheptyl 4-[4'-(undec-10-enyloxy)biphenyl-4-carbonyloxy]benzoate (**4k**). Yield 1.2 g (67%), Cr 30.6 SmC* 106.1 SmA 125.9 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.24 (2H, d), 8.14 (2H, d), 7.71 (2H, d), 7.60 (2H, d), 7.32 (2H, d), 7.01 (2H, d), 5.86 (2H, m), 5.15 (1H, m), 4.95 (2H, t), 4.05 (2H, t), 2.05 (2H, m), 1.80 (2H, m), 1.60-1.25 (25H, m), 0.90 (3H, t). IR (KBr) $\nu_{\max}$ 3010–2800, 1725, 1710, 1600, 1270, 1200, 1160, 1120, 830, 760 cm^{-1}. MS *m/z* 600 (M^{+}), 470, 349 (100%), 307, 209, 197, 141, 115, 83, 69, 55, 45. $[\alpha]_{\mathrm{D}} = +16.0^{\circ}$.

(R)-(+)-1-Methylheptyl 4'-[4'-(undec-10-enyloxy)biphenyl-4-carbonyloxy]biphenyl-4-carboxylate (**4l**). Yield 0.6 g (43%), Cr$_1$ 46.6 Cr$_2$ 102.4 SmC* 172.0 SmA 214.7 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.27 (2H, d), 8.13 (2H, d) 7.65 (8H, m), 7.35 (2H, d), 7.00 (2H, d), 5.82 (2H, m), 5.19 (1H, m), 4.98 (2H, m), 4.02 (2H, t), 2.05 (2H, m), 1.80 (2H, m), 1.55–1.20 (25H, m), 0.89 (3H, m). IR (KBr) $\nu_{\max}$ 3080, 2920, 2870, 1750–1730, 1600, 1500, 1280, 1200, 1120, 760 cm^{-1}. MS *m/z* 518 (M^{+}), 380, 249, 241, 228 (100%), 197, 168, 152, 139, 115, 69, 55. $[\alpha]_{\mathrm{D}} = +14.1^{\circ}$.

(S)-(−)-2-Methylbutyl 4-[4'-(undec-10-enyloxy)phenyl-1-carbonyloxy]benzoate (**4m**). Yield 0.9 g (21%), Cr 45.8 SmC* 51.3 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.15 (2H, d), 8.11 (2H, d), 7.29 (2H, d), 6.98 (2H, d), 5.80 (2H, m), 4.95 (1H, m), 4.20 (2H, m), 4.10 (2H, t), 2.10 (2H, m), 1.85 (2H, m), 1.60–1.20 (13H, m), 1.00 (6H, m). IR (KBr) $\nu_{\max}$ 3000–2820, 1740–1710, 1600, 1500, 1270, 1210, 1160, 780 cm^{-1}. MS *m/z* 480 (M^{+}), 393, 273, 231, 147, 133, 121 (100%), 107, 93, 65, 55. $[\alpha]_{\mathrm{D}} = -2.0^{\circ}$.

(S)-(−)-2-Methylbutyl 4-[4'-(undec-10-enyloxy)phenyl-1-carbonyloxy]biphenyl-4-carboxylate (**4n**). Yield 1.2 g (45%), Cr 67.9 SmC* 104.3 SmA 151.4 N* 153.5 BP 155.1 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.17 (2H, d), 8.12 (2H, d), 7.69 (2H, d), 7.65 (2H, d), 7.31 (2H, d), 6.98 (2H, d), 5.56 (2H, m), 4.95 (1H, m), 4.2 (2H, m), 4.05 (2H, t), 2.05 (2H, m), 1.85 (2H, m), 1.60–1.25 (13H, m), 1.00 (6H, m). IR (KBr) $\nu_{\max}$ 3000–2820, 1720, 1710, 1600, 1260, 1160, 760 cm^{-1}. MS *m/z* 556 (M^{+}), 470, 283, 273 (100%), 214, 196, 133, 121 (100%), 107, 93, 55, 45. $[\alpha]_{\mathrm{D}} = -1.6^{\circ}$.

(S)-(−)-2-Methylbutyl 4-[4'-(undec-10-enyloxy)biphenyl-4-carbonyloxy]benzoate (**4o**). Yield 1.0 g (30%), Cr 50.2 SmC* 128.8 SmA 171.6 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.24 (2H, d), 8.16 (2H, d), 7.71 (2H, d), 7.60 (2H, d), 7.33 (2H, d), 7.00 (2H, d), 5.85 (2H, m), 5.00 (1H, m), 4.35 (2H, m), 4.00 (2H, t), 2.05 (2H, m), 1.85 (2H, m), 1.50–1.25 (13H, m), 1.00 (6H, m). IR (KBr) $\nu_{\max}$ 3000–2820, 1730. 1710, 1600, 1260, 1200, 1060, 760 cm^{-1}. MS *m/z* 556 (M^{+}), 534, 469, 349 (100%), 279, 197, 69, 55. $[\alpha]_{\mathrm{D}} = -3.2^{\circ}$.

(R)-(−)-2-Methylbutyl 4'-[4'-(undec-10-enyloxy)biphenyl-4-carbonyloxy]biphenyl-4-carboxylate (**4p**). Yield 0.9 g (38%), Cr$_1$ 72.5 Cr$_2$ 104.4 SmC* 225.2 SmA 288.0 I (°C). ^{1}H NMR (CDCl$_3$) δ 8.26 (2H, d), 8.13 (2H, d), 7.75–7.60 (8H, m), 7.36 (2H, d), 7.01 (2H, d), 5.85 (2H, m), 5.00 (1H, m), 4.20 (2H, m), 4.05 (2H, t), 2.10 (2H, m), 1.85 (2H, m), 1.65–1.20 (13H, m), 1.00 (6H, m). IR (KBr) $\nu_{\max}$ 3100–2880, 1730. 1710, 1600, 1280, 1200, 1060 cm^{-1}. MS *m/z* 632 (M^{+}), 570, 545, 349 (100%), 273, 197, 121, 55. $[\alpha]_{\mathrm{D}} = -2.6^{\circ}$.

5.2.13. *Polymerisation of cyclic siloxane tetramers by hydrosilylation*

Speiers catalyst was first prepared by dissolving hydrogen hexachloroplatinate(IV) (0.10 g) in dry isopropanol (1 ml); dry toluene (9 ml) was added, with shaking, and the solution was stored in the dark at 4°C.

To prepare the cyclic siloxane tetramers, the appropriate cyclic siloxane tetramer backbone, the appropriate terminal alkene monomer and 4–6 drops of the prepared Speiers catalyst solution were dissolved in dry toluene (15 ml) and heated, with stirring, at 60°C under anhydrous conditions for 24–48 h (see tables 7 and 8 for reagent weights). The progress of the reaction was monitored using IR spectroscopy by examining the spectra in the region of 2155 cm^{-1} (Si–H fingerprint absorption). The disappearance of this band indicated completion of the substitution. Upon completion, the toluene was removed

Table 7. Experimental data for the 2MB series cyclic siloxane tetramers.

Polymer	Polysiloxane/g	Mesogen/g	Yield/g (%)
C4,4e	0.132	0.90	0.54 (52)
C4,4f	0.111	1.00	0.24 (24)
C4,4g	0.052	0.48	0.23 (50)
C4,4h	0.067	0.70	0.52 (74)
C4,4m	0.073	0.65	0.51 (77)
C4,4n	0.048	0.50	0.22 (44)
C4,4o	0.039	0.40	0.40 (98)
C4,4p	0.034	0.40	0.30 (75)

Table 8. Experimental data for the 2MH series cyclic siloxane tetramers.

Polymer	Polysiloxane/g	Mesogen/g	Yield/g (%)
C4,4a	0.108	0.90	0.75 (82)
C4,4b	0.062	0.60	0.41 (68)
C4,4c	0.060	0.60	0.45 (75)
C4,4d	0.019	0.21	0.10 (46)
C4,4i	0.045	0.40	0.10 (30)
C4,4j	0.037	0.40	0.15 (37)
C4,4k	0.046	0.50	0.15 (30)
C4,4l	0.024	0.30	0.23 (78)

by distillation under reduced pressure and the cyclic tetramer was reprecipitated by dissolving the tetramer in the least amount of dry dichloromethane and then adding dry methanol (at least four times the volume of the dichloromethane). The resulting cyclic tetramer suspension was then centrifuged at 4500 rpm. for 30 min, the liquid decanted off, and the process repeated until TLC analysis (silica gel, 9 : 1 mixture of petroleum fraction b.p. 40–60°C: diethyl ether) showed a pure sample (single spot, with no monomer remaining). The cyclic tetramer was then re-dissolved in dichloromethane and filtered using a disposable syringe filter (PTFE membrane 0.45 µm) to remove any particulates; the solvent was carefully removed under reduced pressure and the tetramer dried *in vacuo*.

Tables 7 and 8 show the quantities of the mesogenic side groups and cyclic siloxane backbone used in the preparation of the cyclic siloxane tetramers, along with the weight and percentage yields for each of the hydrosilylation reactions. The transition temperatures for the cyclic siloxane tetramers in the 2MB series are given in tables 3 and 4 and for the 2MH series tetramers in tables 5 and 6.

^{1}H NMR data for these tetramers are not shown individually. All the polymers showed ^{1}H NMR traces similar to the mesogenic side group with the loss of the alkenic protons $d = 5.85$ and $d = 5.00$, and included an extra signal for the methyl protons attached to the ring, $d = 0.10$.

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