Polyhedral Liquid Crystal Silsesquioxanes

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Synthetic routes towards monodisperse polyhedral liquid-crystalline silsesquioxanes are described. The liquid-crystalline phase behaviour of these structurally uniform materials, with various silsesquioxane core and mesogenic side-chain structures, were analysed and compared with those of related oligomeric and polymeric materials. Common features of the solid-state behaviour of these organic/inorganic hybrids, which form self-organized structures in their soft-matter states, were identified. Copyright © 1999 John Wiley & Sons, Ltd.

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INTRODUCTION

Although polyhedral silsesquioxanes have been known for a considerable time[1–3] and are the subject of several reviews,[4–12] only fairly recently has their use as components of liquid-crystalline systems become the focus of attention[13–20].

The materials to which polyhedral LC silsesquioxanes currently show the closest resemblance in chemical structure are rod-like organic mesogens terminally substituted with alkylsiloxane groups or similarly substituted siloxane rings, stars and linear polysiloxanes.

For low-molar-mass materials the chemical structure defines the occurrence and the stability range of liquid-crystal (LC) phases. For linear side-chain polymers it is well established that for a given pendant side-chain the LC properties are strongly dependent on size (degree of polymerization),

polydispersity and the tacticity of the backbone; this highlights the importance of well characterized materials to the understanding of their phase behaviour[21,22].

The use of silsesquioxanes as molecular scaffolding for liquid-crystalline systems rests on their discrete molecular structure. It allows for *monodisperse* backbone entities, which have a defined molecular geometry in which the core provides a compact, fixed directionality to the resulting molecule. This eliminates a major problem in the investigation of the side-chain liquid-crystal polymer systems, namely the dependency of liquid-crystal properties on polydispersity and tacticity, while combining the main advantages of both side-chain LC polymers, i.e. their robustness and processability, with the advantages of low-molar-mass systems, i.e. their fast response to external stimuli.

METHODS OF SYNTHESIS

A liquid-crystalline silsesquioxane is constituted of the following components: the silsesquioxane core **a**; an attachment linking the hydrocarbon spacer to the inorganic core, possibly *via* a silicon-organic spacer **b**; the hydrocarbon spacer **c** separating the mesogen and the polyhedral centre; and finally the mesogenic group **d**, as shown in Fig. 1, a space filled structure is shown in Fig. 2.

Although it is conceptually not necessary, all polyhedral silsesquioxane liquid crystals reported so far have been synthesized by a convergent route, in such a manner that the silsesquioxane core and the liquid-crystalline side-chain are synthesized separately and fused in the last step.
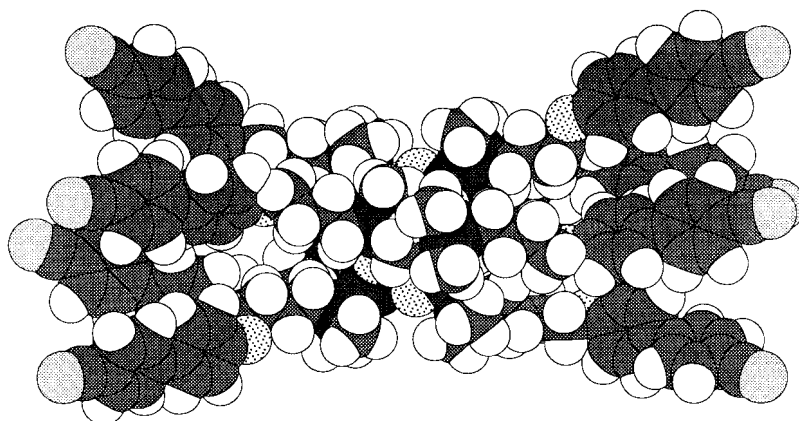
Cores

The core structures discussed in this contribution are depicted in Fig. 4. The functionalization of the silsesquioxane cores is relatively difficult and the variety of coupling reactions that can be tolerated by the polyhedral core is rather limited[23–30]. There

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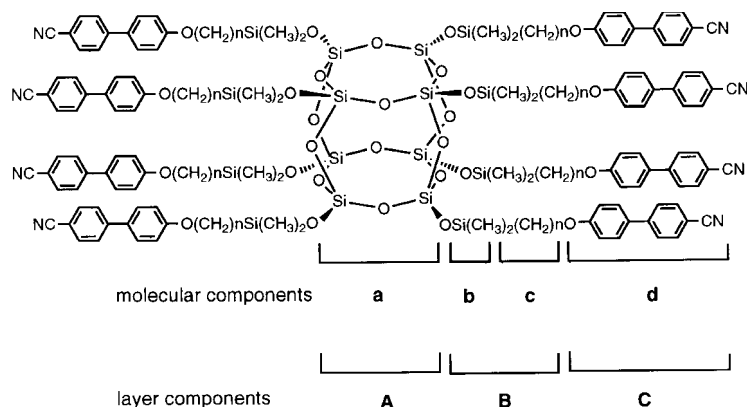
Figure 1 Structure of the elements building up a liquid-crystal silsesquioxane.

Figure 2 Spindle-type structure of liquid-crystalline silsesquioxanes.

are two common pathways to silsesquioxane cores, either *via* controlled hydrolysis of appropriately functionalized trichlorosilanes yielding, a variety of structures depending on the reaction conditions and the work-up, or *via* controlled condensation of silicic acid and subsequent functionalization.

The most frequently used cores are the cubic octasilsesquioxanes. Octa(hydridosilsesquioxane), $Si_8O_{12}H_8$ (T_8H_8) (core **B**) was first synthesized in 1959[31]. The use of this material in the past has been hampered by the lack of an efficient synthesis and the difficulty in separating the oligomers produced in the hydrolysis of Cl_3SiH. However T_8H_8 is now available reproducibly in gram quantities[27,32]. The higher polyhedral oligomers T_{10}, T_{12} and T_{14} have recently been isolated in gram quantities[33] and the separation of T_8–T_{18} by size-exclusion chromato-

graphy (SEC) has been reported.[34] Though there are at present no reports of the use of these cores as scaffolding for liquid-crystal materials, their structure makes them of interest as substrates for novel LC systems.

Octa(hydridodimethylsiloxy)octasilsesquioxane (core **A**) is accessible in gram quantities through a synthetic route *via* the reaction of $[NMe_4]_2[SiO_4]$ with $ClHSiMe_2$[5,9–13,35].

Extensive earlier work[9–12] investigating the reaction conditions which direct the condensation of silicic acid to a particular polyhedral structure highlighted the influence of the size of the alkyl chains in the tetra-alkylammonium hydroxide on the condensation reaction. It was found that the synthesis of trigonal prismatic systems (core **E**) is best achieved using tetraethylammonium hy-

droxide, whereas the octa(dimethylsiloxy)silsesquioxane core **A** is favourably obtained using tetramethylammonium hydroxide as co-reagent and deca(dimethylsiloxy)silsesquioxane (core **D**) is yielded using tetrabutylammonium hydroxide[9–12].

Silylation

The strategy used for the synthesis of liquid-crystal silsesquioxanes has so far proceeded exclusively via a modification of the silsesquioxane cores through hydrosilylation of a terminal olefin, undoubtedly because the similar route to the related liquid-crystal side-chain polyorganosiloxanes is well documented[21,22]. This synthetic route can be followed through two pathways, either by a hydrosilylation reaction of a mesogen containing a terminal alkene group with a hydridosilsesquioxane, or by a hydrosilylation of an alkenylsilsesquioxane with a mesogen terminated with a hydridosilicon functionality.

The systems described here follow the first route and make use of the addition of the Si—H bond of the appropriate hydridosilsesquioxane to the terminal carbon–carbon double bond on the flexible spacer of the mesogen that is to constitute the appended side-chain[36–42]

Hydrosilylation studies using T_8H_8 were first disclosed by Herren and Calzaferri, reporting the synthesis of monosubstituted alkyl and ferrocenyl heptahydridosilsesquioxanes[23–26] using hexachloroplatinic acid as catalyst. They found that in the case of unsubstituted linear alkenes the reaction proceeded exclusively to the α-isomer; for vinylferrocene as reactant a similar result was observed (the assignment of α and β is shown in Fig. 3). This result was confirmed for unsubstituted alkenes[27], but for allyloxy derivatives significant amounts of the branched β-isomer were found[15,29]. For vinyl siloxanes *ca* 21% β-addition occurs and simultaneously a vinyl/H exchange takes place on silicon[27]. However, in the case of allylsiloxanes the regioselectivity of the reaction was found to be

Figure 3 Assignment of α and β addition.

higher as it produced only the linear α-isomer, but the allyl/H exchange process was still present[43].

Similarly, the hydrosilylation of unsubstituted terminal alkenes with $(Si_8O_{12})(OSiMe_2H)_8$ (**A**) yields exclusively the linear α-isomer[44], whereas a conjugated olefin, e.g. vinylferrocene, yields both isomers in an α/β ratio of *ca* 9:1[35].
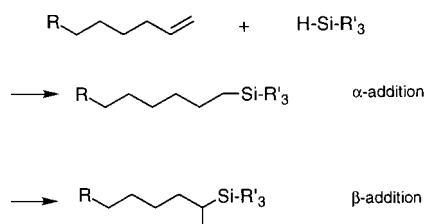
If their LC properties are to be considered, the α and β isomers are expected to show very different properties. If different isomers are present in a material it is a 'liquid-crystal mixture'. Unless the ratio of α/β isomers is known and strictly reproducible, it is very difficult to draw a correlation between the chemical structure and the ensuing physical properties[16–20,45].

We observed that for silsesquioxane cores the addition to the terminal alkene group of the flexible spacer of the mesogen is regiospecific within the limits of detection used, affording only the linear α-isomer, using Karstedt's catalyst at room temperature. The β-addition product is usually identified by a signal in the vicinity of 2.0 ppm in the ^{1}H NMR spectrum due to RSi—CH(R′)—CH$_3$ and by the signal of the Si—C$_{internal}$ upfield from the Si—C$_{terminal}$ in the ^{29}Si NMR spectrum of these materials.

The structural principles of organic low-molarmass rigid rod-like mesogens have been extensively reviewed and discussed (most recently, in Refs 36 and 37), and will not be addressed here. Metalcontaining liquid crystals (metallomesogens) are a much younger addition to the field of liquid crystals, and the role of the metal centre in the formation of stable mesophases is not yet fully explored[38].

A somewhat delicate synthetic task is posed by metallomesogens. As the side-chain contains a potentially reactive metal centre, the method of functionalization of the cage not only needs to be tolerant of the cage and the functional groups of the mesogen, but also designed to avoid any possible interference of the metal in the process. This is particularly relevant for the hydrosilylation reaction: in a metal-catalysed reaction in the presence of another metal, the choice of catalyst is of crucial importance, and the mildest experimental conditions should be attained in order to avoid side reactions involving the metal centre.

There are very few studies involving the influence of the type of catalyst on the conversion of polyhedral hydridosiloxane cores in the presence of liquid-crystalline groups. Recently, it appears that the very robust Speier's catalyst (H_2PtCl_6 in isopropanol) has been employed less often than

during the initial period of the synthesis of siloxane groups containing liquid-crystalline side-chains. The use of various cyclopentadienylplatinum derivatives or Karstedt's catalyst (platinum–(divinyltetramethyldisiloxane), 3–3.5% platirum concentration in xylene) allow for considerably lower reaction temperatures, but an increased sensitivity of the catalyst to hydrolysis has to be taken into account. However, under most circumstances this is compensated by the good conversion results at room temperature.

In our experiments we observed that Karstedt's catalyst was very effective at room temperature, requiring reaction times of 1–3 h, without any sign of interference with the metal complexes or other LC side-chains used by us.

To ensure complete reaction of the hydridosilsesquioxane with the mesomorphic alkene, a small excess of the alkene is required. We have used typically a 10% molar excess of the alkene for linear terminal olefins and cyanobiphenyl derivatives; however, for derivatives of lower solubility, e.g. metallomesogens, a larger excess is advantageous in order to ensure complete conversion. Incomplete conversion leaves unreacted Si-H bonds which, when heated in the solid state, can react with other functional groups causing cross-linking and degradation of the sample.

Upon completion of the reaction the very active Karstedt's catalyst is deactivated by addition of a small amount of triphenylphosphine. The deactivation of the catalyst avoids contamination by the deposition of platinum metal. It has been shown that the presence of platinum affects the transition temperatures and the electro-optical behaviour[21,22].

PURIFICATION

As shown for side-chain mesogenic polysiloxanes[21,22], one of the difficulties encountered in the purification of the LC silsesquioxanes is that, even in the case of complete conversion of the Si—H moieties, effective removal of the excess alkene used is required in order to obtain reproducible transition temperatures in materials from different batches.

The presence of small amounts of isomeric alkenes making up the hydrocarbon spacer in a silsesquioxane oligomer might bring about a decrease in transition temperatures and/or a modification of the type of mesophase exhibited.

We have found column chromatography unsuit-

able for purification so far, as silica gel does not seem to provide the desired separation, whereas the use of flash-grade silica gel tends to cause irreversible adsorption of the samples onto the support.

The usual work-up procedure is the precipitation of a solution of the silsesquioxane in dichloromethane into a large volume of methanol (volume/volume ratio $\simeq$1:10); this procedure is repeated until no monomer is detected in the silsesquioxane by thin-layer chromatography. The merits of TLC detection in the course of removal of alkenes have been described in detail[39,40].

Gel permeation chromatography is particularly useful to ascertain the monodispersity of the materials, and it provides a first-hand indication. However, due to the absence of calibration standards of similar structures, the absolute values measured have to be treated with some caution.

LIQUID CRYSTAL PROPERTIES

Polyhedral LC silsesquioxanes can be viewed as an element in the series of materials ascending from low-molar-mass liquid-crystal to linear side-chain polymers. In order to achieve such a structural arrangement the mesogens of one polyhedral molecule are aligned antiparallel along one axis, as depicted in Fig. 1 and Fig. 2, giving a spindle type of structure. This leads to a structure in which the polyhedral cores are situated in the centres of the layers, separated from the mesogenic cores by the mainly hydrocarbon layer of the spacer. This idealized concept of a fluid-like layered phase leads to a picture of a sequence of layers of silsesquioxanes (A), methylene groups (B) and mesogenic, usually aromatic, cores (C) in an ABCCBA sequence (Refs 16 and 17 and references therein, and Ref. 44; see also Fig. 1). For the description and understanding of the liquid-crystalline phase behaviour of these materials, their essentially trichotomous molecular structure has to be taken into consideration. The type and stability of the liquid-crystalline phase will be determined by the structure of the mesogenic side-chains and the structure of the organo-silicon core.

In order to evaluate the solid-state properties of these materials they have to be compared with structurally related oligomeric and polymeric liquid crystals. The chemical structures of the side-chains discussed are shown in Fig. 5.

For side-chain LC polymers it has been estab-
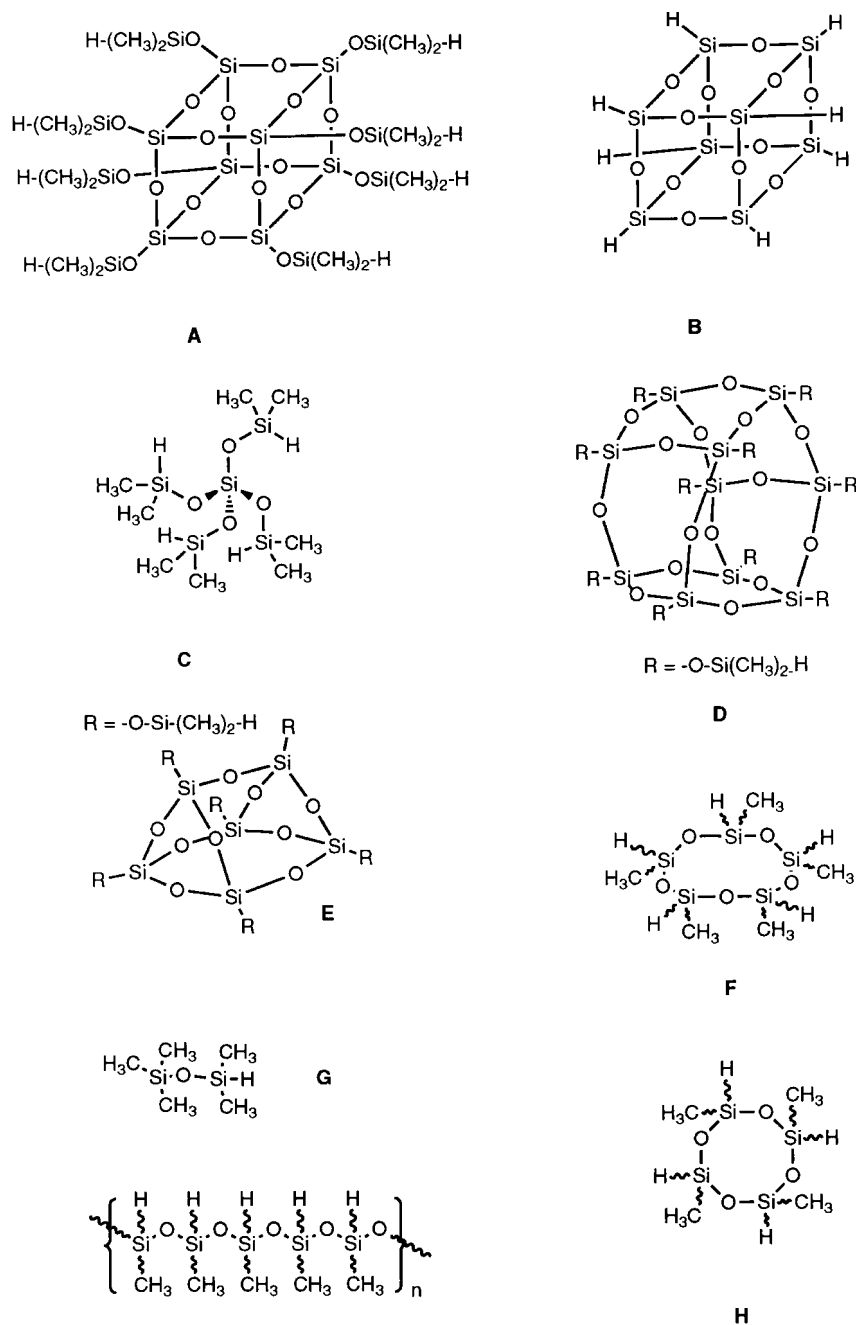
Figure 4 Structures of the silicon-containing cores.

lished that for a given side-chain the phase transition temperatures increase with increasing numbers of repeat units, until a plateau is reached above which the transition temperatures are constant[21,22]. Depending on the polydispersity of the material and the structure of the backbone, this value is reported to be obtained between 12 and 30 repeat units. Thus in the region of degrees of polymerization between 2 and 12 the changes in properties are the largest.

For the attachment of a cyanobiphenyl group as mesogenic core, separated from core **A** by methy-
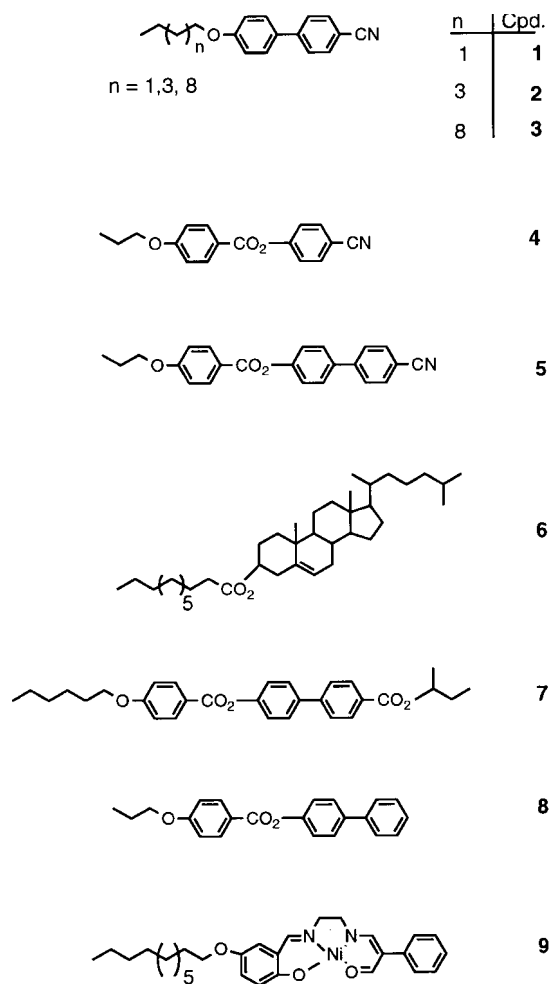
Figure 5 Structures of the liquid-crystalline side-chains.

lene spacers containing more than four methylene groups (side-chains **1**, **2** and **3**) calorimetric studies show that the materials **10**, **11** and **12** exhibit liquid-crystal phases[16,17]. The values for the transition temperatures, and the associated enthalpies and entropies for the second heating cycles, of each compound are listed in Table 1. Thermal polarized light transmission microscopy reveals the formation of a focal-conic defect texture, with hyperbolic and elliptical lines of optical discontinuity, as each material is cooled from the amorphous liquid into the liquid-crystal state. These observations classify the high-temperature liquid-crystal phase of each material as smectic A. Mechanical shearing of the specimens in the microscope shows that the high-temperature mesophase flows easily and has a relatively low viscosity. In addition, the short time

required to form focal-conic defect textures on cooling from the isotropic liquid indicates that the compounds have properties more in keeping with low-molar-mass materials than with polymers.

Increasing the number of methylene units in the spacer chain between the cyanobiphenyl and silsesquioxane core units from four to 11 carbon atoms results in the isotropization temperature being increased from 93.9 (**10**) to 128.5 °C (**12**), the LC phase preceding the isotropization being a smectic A phase.

For the structurally related materials **13**, **14** and **15** with a cross-shaped tetrakis(dimethylsiloxane) core **C**, a similar trend in the development of the phase behaviour could be observed; the isotropization temperature is increased from 88.7 (**13**) to 129.7 °C (**15**) as the spacer increases from four to eleven methylene units[16,17].

Comparison with cyclic materials based on tetramethylsiloxane rings **F** reveals that the transition temperatures are roughly similar for compound **16**[44], which has a spacer of six methylene groups. It shows the transition from the smectic A phase to the isotropic phase at 118 °C. The material **17** with the spacer of 11 methylene units becomes isotropic at 141.3 °C.

Comparison with linear polymers with a siloxane backbone which exhibit isotropization temperatures of 132 °C for the polymer **18** (side-chain **1**), 166 °C for **19** (side-chain **2**) and 157 °C for **20** (side-chain **3**) showed that they follow a similar pattern to that found for the oligomers.

For the oligomeric materials the increase from four to eight side-chains does not affect the transition temperatures significantly, but the silsesquioxane based materials tend to have higher glass transition temperatures. The decrease in the value of the glass transition temperature with increasing spacer length can be attributed to the plastifying effect of the alkyl groups. Additionally the silsesquioxane-based materials with the longer spacers exhibit a rich, though not yet fully explored, crystalline polymorphism at lower temperatures.

The values for the isotropization enthalpy, reduced molar entropy ($\Delta S_{mol}/R$) and the reduced molar entropy per side-chain ($\Delta S_{mol}/nR$) for the silsesquioxane systems shown in Table 2 indicate that an increase of the size of the enthalpy peak occurs with increasing spacer length, suggesting that there is an increase in the ordering of the molecules within the liquid-crystal phase. This conjecture is supported by the fact that there is also an increase in the calculated reduced molar entropy ($\Delta S_{mol}/R$), from 4.35 (**10**) to 9.68 (**12**), as the series

Table 1. Transition temperatures (°C) and enthalpy data [ΔH (J g^{-1}) ΔC_p (J g^{-1} K^{-1})]

Compound	Core	Side-chain	T_g (°C) [ΔC_p (J g^{-1} K^{-1})]	Transitions [a] (°C) [ΔH (J g^{-1})]
10	**A**	**1**	11.0 [0.22]	S$_A$ 93.9 [4.31] Iso
11	**A**	**2**	3.0 [0.32]	S$_1$ 22.5 [0.19] S$_A$ 116.5 [5.40] Iso
12	**A**	**3**	−7.5 [0.28]	cr 34.4 [10.2] S$_2$ 54.6 [0.77] S$_3$ 64.5 [1.20] S$_A$ 128.5 [8.66] Iso
13	**C**	**1**	−9.6 [0.34]	S$_A$ 88.7 [4.85] Iso
14	**C**	**2**	−14.7 [0.36]	S$_A$ 118.7 [7.83] Iso
15	**C**	**3**	−6.3 [0.31]	cr 38.7 [18.29] (S$_C$ 42 [—]) S$_A$ 129.7 [5.40] Iso
16[b]	**H**	**2**	57	S$_A$ 118 [5.6] Iso
17	**H**	**3**	—	cr 59.9 [25.7] S$_A$ 141.3 [11.1] Iso
18[c]	**I**	**1**	28	S$_A$ 132 Iso
19[c]	**I**	**2**	14	S$_A$ 166 Iso
20[c]	**I**	**3**	−1	S$_C$ 48 S$_A$ 157 Iso

[a] S1, S2, S3 are smectic or soft-crystal phases.
[b] From Ref. 44.
[c] From Refs 21 and 22.

Table 2. Reduced entropies ($\Delta S_{mol}/nR$) and reduced entropies per side-chain ($\Delta S_{mol}/nR$)

Compound	Core	Side-chain	$\Delta S/R$	$\Delta S/nR$
10	**A**	**1**	4.35	0.54
11	**A**	**2**	5.50	0.69
12	**A**	**3**	9.68	1.21
13	**C**	**1**	2.14	0.54
14	**C**	**2**	3.46	0.87
15	**C**	**3**	6.33	1.58

tetrahedral and for the silsesquioxane-based core. For all the materials, investigated an increase in spacer length leads to an increase in the values for the reduced molar entropy per side-chain. The rise for the silsesquioxane-based compounds is however less than that of the smaller tetrahedral materials.

X-ray diffration can be used to elucidate the LC phase structure further. The high-temperature liquid-crystal phase of the materials **10**–**12** showed an X-ray diffraction pattern which was obtained from fibre samples recorded in Lindemann tubes and found to be typical of the smectic A phase[8]. The values detected are listed in Table 3. The diffuse wide-angle halo at 4.4–4.5 Å is typical for the lateral distance between mesogenic units. Diffuse reflections at 8.2 Å for the tetrahedral materials and of 12.0–13.2 Å were attributed to the periodicity of the arrangement of the silicon-containing cores[1–3,5,8].

is ascended. For the related tetrahedral systems the values of the reduced molar entropy increase from 2.14 for **13** to 6.33 for **15**. Dividing these values by the number of side-chains present in the molecule ($\Delta S_{mol}/nR$) reveals that for the materials with the shortest spacer similar values of 0.54 occur for the

Table 3. The *d*-spacings (Å) determined by X-ray diffraction for compounds 10–12

Compound	Side-chain	T (°C)		*d*-spacings (Å)		
10	**1**	25.0	4.5	11.3	—	32.2
11	**2**	25.0	4.5	12.0	17.6[a]	35.4[a]
12	**3**	75.0	4.5	13.2	21.6	43.1
12	**3**	85.0	4.5	13.2	21.4	42.8
12	**3**	100.0	4.5	13.2	21.3	42.8
12	**3**	110.0	4.5	13.2	21.0	42.1
12	**3**	120.0	4.5	13.2	21.0	42.1
12	**3**	125.0	4.5	13.2	21.0	42.1

[a] Reflections are very weak.

Table 4. Transition temperatures (°C) (Ref. 14) and (Ref. 15)

Compound	Core	Side-chain	T_g (°C)	Transitions (°C)
21	B	4	—	cr 119 S_A 146 Iso
22	B	5	102	S_X 127 S_A >300 Iso
23	A	6	46	cr 128 S_A 157 Iso
24	B	6	108	cr 108 S_A 160 Iso
25	D	6	51	cr 122 S_A 164 Iso
26	E	6	30	S_X 37 S_A 142 Iso
36	B	8	—	cr 90 S_X 184 N Iso

Table 5. Transition and glass transition temperatures (°C), specific heats ΔC_p (J g^{-1} K^{-1}) and transition enthalpies ΔH (J g^{-1}) of materials derived from side-chain 7, determined by DSC measurements (10 °C min^{-1})

Compound	Core	T_g (°C) [ΔC_p (J g^{-1} K^{-1})]	Phase transitions [a] (°C) [ΔH (J g^{-1})]
8	Monomer	—	cr 78.5 S_C 106.1 [0.68] S_A 157.2 [2.93] N 168.9 [1.51] Iso
27	C	−8.4 [0.47]	S_{Ca} 125.0 [0.13] S_C 154.4 [0. 1] S_A 164.4 [—][b] Iso
28	H	10.3 [0.54]	S_Xb 69.5 [1.03] S_C 184.2 [—][b] N 193.3 [8.0] Iso
29	F	11.2 [0.37]	S_C 182.5 [—] S_A 188.7 [6.82] Iso
30	E	11.5 [0.14]	S_C 191.5 [2.1] Iso
31	B	—	cr 143.0 [21.1] S_C 208.0 [0. 2] S_A 214.0 [6.4] Iso
32	I	19.0 [0.15]	$S4_C$ 223.5 [0. 1] S_A 234.3 [5.33] Iso

[a] S_X is an unresolved phase.
[b] Unresolvable by DSC.

The values calculated from the small-angle reflections observed for the *d*-spacings of the smectic layers of the silsesquioxane materials listed in Table 3 of 32.2 for **10** to 43.1 Å for **12** at 25 °C are consistent with a structure where the silicon-containing cores are located in the central regions of the layers, and there is some overlap of the terminal cyanobiphenyl groups[8,16,17]. This classifies the high-temperature smectic phase as a smectic A$_d$ (S$_{Ad}$) phase.

The situation is more complex, however, for the tetrahedral material **15**, for which on cooling the occurrence of a smectic C phase preceding crystallization was observed. X-ray diffraction data of this compound showed that at 70 °C in the smectic A phase an arrangement requiring two sublattices is required. After 24 h of annealing reflections of roughly similar intensities relating to periodicities of 38.7 and 46.7 Å could be observed. This can be accommodated with a phase structure in which some of the mesogens overlap completely and some only partly[17].

The influence of the stiffness of the mesogenic core on the transition temperatures has been demonstrated by Kreuzer *et al.*[14] for materials based on the core **A**, as has been shown for mesogens **4** and **5** terminated with aromatic cyano groups leading to compounds **21** and **22**. The transition temperatures are listed in Table 4.

The variation in the core structure, employing cores **E**, **A** and **D** and thus resulting in materials **23**, **24** and **25**, is accompanied by an increase in the isotropization temperature from 142 to 164 °C[14]. An interesting feature is the occurrence of crystalline phases as the number of branches rises from six to ten while the structure of the mesogens is retained. It can be assumed that the crowding of the mesogens in the vicinity of the silsesquioxane cores leads to additional ordering in the alkyl chains. A comparison of the core structures **A** and **B** revealed for the mesogen **6** that the isotropization temperatures are relatively unaffected by the presence of the dimethylsiloxane group in **A**. The isotropization temperature from the smectic A phase is reported[14] to be 157 °C for **24** and 160 °C for **26**. The pressure of the dimethylsiloxane depresses the crystallization by 20 °C, from 128 °C in **26** to 108 °C in **24**.

The structure of the materials derived from the side-chain **7** which promotes the formation of tilted phases and the silicon-containing cores; the results

are listed in Table 5[20]. The type of core employed influences the phase behaviour considerably through its geometry, the concentration of stereo-isomers, its tendency to phase-separate and the number of branches present in the molecules.

To fit cyclic liquid-crystalline materials made of small rings consisting of different isomers into smectic phases, they have to be inscribed in a cylindrical (spindle-shaped) structure, with the smallest radius in the core (the area of the siloxanes) and the largest at the terminal groups of the molecule. Due to the limited number of mesogens per core, one molecule cannot fill the enveloping cylinder. It has to be filled by side-chains of other molecules.

Low glass transition temperatures (T_g) and low viscosites can be explained in this model as a result of the flexibility of the core and gaps in the cylinder. Increasing the diameter of the core from four siloxane groups (**H**) in **28** to five (**F**) in **29** leads to an increase in the number of gaps. The glass transition temperature is not much affected by this increase in disorder, but the transition temperatures of the mesophases decrease and a highly ordered phase present (smectic X) is lost altogether.

The use of hexasilsesquioxane **E** or octasilsesquioxane cores **B**, leading to materials **30** and **31**, where the gaps in the cylinder are filled, results in an increase in the mesophase stability, which is not much lower than in material **32** where the mesogen **7** is attached to a much larger linear polymer **I**.

The compound **27** with the tetrahedral core **C** has a markedly different phase behaviour from the other materials; this can be rationalized in the following manner. There is an odd number of atoms separating the two pairs of anti-parallel oriented mesogens. For the material in a layered phase this favours a minimum-energy conformation of the molecules where two pairs of mesogens of one molecule are not aligned parallel but lie at an angle. This distinguishes this type of materials from cuboid systems (cores **A, B**) where an even number of atoms separates anti-parallel mesogens. The effects of the odd–even effect in liquid crystals are discussed extensively elsewhere (see Refs 21, 22, 36 and 37, and references therein).

Due to its crowded central core (**C**) with its eight methyl groups, the glass transition and clearing temperature are much lower than in all the other materials. Due to the possibility of intramolecular interactions facilitated through the close proximity of the side-chains, that are liquid-crystalline phases can be realized similar to those found for the other materials. Additionally, an alternating smectic C

(S_{Ca}) phase occurs at temperatures below 125 °C and can be identified by its transition enthalpy at the transition from the smectic C phase ($\Delta H = 0.13$ J g^{-1}), and by two and four brush defects in its *Schlieren* texture which are associated with the S_{Ca} phase. This texture could not be observed for the other materials.

The use of a metallomesogen as a side-chain opens the possibility of generating materials which are predominantly inorganic in the structure of their scaffolding. The inclusion of metals in mesogens makes it possible to combine properties associated with metallic materials, e.g. magnetism and/or conductivity, with liquid-crystalline phase behaviour.

The addition of a pentamethylsiloxane unit **G** to side-chain **9** results in compound **33**, where the stability range of the smectic A phase is enhanced to 240 °C[45]. The results are listed in Table 6. Fusing **9** to a tetrameric cyclic siloxane ring system results in material **34**, consisting of several stereoisomers, and leads to a further enhancement of the isotropization temperature to 296 °C. This is the first example of a polyhedral silsesquioxane with appended metallomesogens[18]. The nickel-modified compound **35** has been prepared by hydrosilylation of the non-symmetrical, diamagnetic, square-planar nickel complex **9** with $(Si_8O_{12})(OSiMe_2H)_8$ (**A**). Investigation of its solid-state properties revealed that the crystalline state is enhanced up to 219 °C, when decomposition sets in.

Systems where more than one type of mesogen is attached to a silsesquioxane core or not all of the reactive Si—H groups are converted are attractive because they promise to offer tailoring of the LC properties by the use of appropriately selected side-chains. Preparatively, the problem of controlling the uniformity of the products can be envisaged to be difficult.

The few reports available[14] indicate that if suitable side-chains of the type of **8** are included, crystalline phases are suppressed and glass transitions appear. Additionally, for such a system **36**

Table 6. Transition temperatures (°C) determined by DSC measurements (10 °C min^{-1}) for the 9 and 33–35

Compound	Core	Side-chain	Phase transitions (°C)
9	—	**9**	cr 181 S_A 190 Iso
33	**G**	**9**	cr 184 S_A 240 Iso
34	**H**	**9**	cr 196 S_A 296 dec
35	**A**	**9**	cr 219 dec

consisting of core **B** and side-chain **8** where four of the eight Si—H groups were reacted, the first nematic phase in LC silsesquioxane materials could be observed,[15] with a stability range of the nematic phase up to 184 °C (see Table 4). Altogether the phase behaviour of these systems seems to become close to that of cyclic siloxanes[46].

For materials where two rigid side-chains are employed, the phase transition temperatures seem to depend strongly on the core structure, with the systems containing more aromatic cores in the side-chain having higher transition temperatures.

EXPERIMENTAL

Synthesis of octakis[4-cyano-4′-(6-dimethylsiloxy)hexyloxy-biphenyl]octasilsesquioxane (11)

A solution of toluene (20 ml), 4-cyano-4′-(5-hexenyloxy)biphenyl (0.55 g, 1.58 mmol) and 10 ml of a 3.0 –3.5 % solution of Karstedt's catalyst dissolved in xylene was gently aerated for 20 s, then a solution of *octakis* (hydrodimethylsiloxy)octasilsesquioxane (0.1 g, 0.098 mmol) in dry toluene (10 ml) was added dropwise at room temperature over a period of 1 h. A few minutes after the addition was complete no Si—H band (2142 cm^{-1}) could be detected by IR spectroscopy. A spatula-tipful of triphenylphosphine was added in order to convert the catalyst to the less reactive triphenylphosphine complex and the solution was concentrated under reduced pressure. The oligomeric material was isolated by precipitation in methanol. The product was separated by filtration, and purified by repetitive precipitation from methanol until no monomer could be detected by chromatographic methods. Recrystallization from pentane yielded 0.31 g of **2** (85%).

Spectral data: IR (KBr): v = 3020 (Ar—H), 2940 (C—H), 2220 (C≡N), 1600 (Ar), 860 cm^{-1} (C—H); ^{1}H NMR (270 MHz, CDCl$_3$, TMS): δ = 7.65 (m, 4H, Ar—H), 7.52 (m, 2H, Ar—H), 6.95 (m, 2H, Ar—H), 3.93 (tr, 2H, Ar—O—CH$_2$), 1.75 (m, 2H, O—CH$_2$—CH$_2$), 1.45 (m, 6H, CH$_2$—CH$_2$—CH$_2$), 0.62 (tr, 2H, CH$_2$—Si), 0.14 (s, 6H, (CH$_3$—Si); ^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 0.01 (CH$_3$—Si), 18.14 (CH$_2$—Si), 23.49, 26.31, 24.78, 33.75, (CH$_2$—CH$_2$—CH$_2$), 67.44 (CH$_2$—O), 110.82 (Ar C4′, C—CN), 115.19 (Ar C3, C$_5$), 126.89, 128.48 (Ar C$_2$, C$_6$, C$_2$′, C$_6$′), 131.56 (Ar C$_1$), 132.49 (Ar C$_3$′, C$_5$′), 144.71 (Ar

C$_1$′), 160.11 (Ar C$_4$, O—C), 118.87 (CN); ^{29}Si NMR (53.5 MHz, CDCl$_3$, TMS):δ = 12.34 (Si—CH$_3$), −108.8 (Si—(O)$_4$—).

Octakis(([8-(3-(10-decyloxydimethylsiloxy)-6-hydroxyphenyl)-2-phenyl-4,7-diazocta-1,3,7-trienato](2-)nickel(II)))octasilsesquioxane (35)

Nickel(II) complex **9** (0.5105 g, 1.01 mmol) was added to a toluene solution (50 ml) containing 10 μl of a 3–3.5% solution of bis(divinyltetramethyldisiloxane)platinum(0) in xylene, and the whole was stirred (1 h) at room temperature. A gentle stream of air was blown through the red solution for a few seconds. A solution of octa(hydrodimethylsiloxy)octasilsexquioxane (0.1017 g, 0.10 mmol) in toluene (20 ml) was added dropwise over a period of 2 h. A brown–red solid separated as the addition progressed. After a further 1 h, the IR spectrum of the reaction mixture showed complete conversion. At this point a few crystals of triphenylphosphine were added to deactivate the catalyst. The ochre-red solid was filtered off and dried *in vacuo*. The solid was washed with tetrahydrofuran to remove any unreacted monomer, dissolved in dichloromethane (5 ml) and filtered through a Pasteur pipette loaded with Hyflo (filter aid) to remove any platinum(0) residues. The product was precipitated out of solution by addition to rapidly stirred methanol (750 ml). This procedure was repeated until the solution showed no TLC-detectable amount of monomer. The ochre-red solid was filtered off and dried *in vacuo*. [yield 0.2717 g (53%).]

Analysis: Calcd for C$_{249}$H$_{328}$O$_{44}$N$_{16}$Si$_{16}$Ni$_{16}$: C, 56.97; H, 6.52; N, 4.42. Found: C, 55.39; H, 6.38; N, 4.42%. MS (FAB): m/z, no M$^+$ detected; Ni–Si-containing clusters of lower fragments. GPC (CHCl$_3$, polystyrene standard): 5775 (M_w) and a second band at 2M_w. M_n = 5075; M_w/M_n = 1.13. IR (KBr disc; v cm^{-1}): 1607 (vs, sharp; C≡N, C=O and C=C—N coordinated); 1085 (vs, broad; Si—O—Si). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.11 (m, 8H; aromatic C$_6$H$_5$, HC=N, HC=O and NCH=C); 6.83 (m, 1H, H_b); 6.68 (m, 1H, H_a); 6.38 (m, 1H, H_c); 3.74 [t (J = 7 Hz) 2H, CH$_2$O]; 3.30 (S, 4H,N—CH$_2$); 1.68 (m, 2H, CH$_2$—CH$_2$—O); 1.30 [m, 14H, —(CH$_2$)$_7$—]; 0.60 (t (J = 7 Hz) 2H, CH$_2$—Si); 0.13(, 6H, Si—CH$_3$). ^{29}Si{1H} NMR (CDCl$_3$; Cr(acac)$_3$): δ 12.65 (s, Si(CH$_3$)$_2$CH$_2$, M silicon); −108.8 (s, SiO$_3$; Q silicon).

SUMMARY

Studies of liquid-crystal polyhedral silsesquioxane materials have been described, relating to their synthesis, specific problems connected with the nature of the silsesquioxane cage, and the special properties that their geometry imparts to their mesogenic behaviour. The synthesis of these materials is based on a silsesquioxane cage modification process, starting with a suitably functionalized cage, to which the mesogens are attached. All the systems described so far are based on the hydrosilylation reaction of hydrido-silsesquioxanes and mesogenic alkenes.

The liquid-crystalline phase behaviour of these structurally uniform materials is related to that of comparable oligomeric and polymer systems and depends strongly on the structure of the mesogenic side-chains. This allows for the tailoring of glass transition temperatures, the type of liquid-crystalline phases and phase transition temperatures over a wide temperature range. The possibility of including metals in the LC side-chains highlights the versatility in this field of research, which is concerned with the soft-matter state of inorganic/organic hybrids.

REFERENCES

1. A. J. Barry, W. H. Daudt, J. J. Domicone and J. W. Gilkey, *J. Am. Chem. Soc.* **77**, 424 (1955).
2. M. M. Sprung and F. O Guenther, *J. Am. Chem. Soc.* **77**, 3990 (1955).
3. E. Wiberg and W. Simmler, *Z. Anorg. Allg. Chem.* **282**, 330 (1955).
4. M. G. Voronkov and V. I. Lavrent'yev, *Topics Curr. Chem.* **102**, 199 (1982).
5. R. H. Baney, M. Itoh, A. Sakibara and T. Suzuki, *Chem Rev.* **95**, 1409 (1995).
6. F. J. Feher and T. A. Budzichowsky, *Polyhedron* **14**, 3239 (1995).
7. R. Murugavel, A. Voigt, M. G. Walawalkar and H. W. Roesky, *Chem. Rev.* **96**, 2205 (1996).
8. A. Agaskar, *Colloids Surf.* **63**, 131 (1992).
9. D. Hoebbel and W. Wieker, *Z. Anorg. Allg. Chem.* **384**, 45 (1971).
10. D. Hoebbel, W. Wieker, P. Franke and A. Otto, *Z. Anorg. Allg. Chem.* **418**, 35 (1975).
11. D. Hoebbel, A. Vargha, B. Fahlke and G. Engelhardt, *Z. Anorg. Allg. Chem.* **521**, 61 (1985).
12. D. Hoebbel, I. Pitsch, T. Reiher, W. Hiller, H. Jancke and D. Müller, *Z. Anorg. Allg. Chem.* **576**, 160 (1989).
13. C. Zhang and R. M. Laine, *J. Organometal. Chem.* **521**, 199 (1996).
14. F.-H. Kreuzer, R. Mauerer and P. Spes, *Makromol. Chem. Macromol. Symp.* **30**, 215 (1991).
15. A. Sellinger, R. M. Laine, V. Chu and C. Viney, *J. Polym Sci. Part A. Polym. Chem.* **32**, 3069 (1994).
16. G. H. Mehl and J. W. Goodby, *Angew. Chem. Int. Ed. Engl.* **35**, 2641 (1996).
17. G. H. Mehl and J. W. Goodby, *Chem. Ber.* **129**, 521 (1996).
18. I. M. Saez and P. Styring, *Adv. Mater.* **8**, 1001 (1996).
19. I. M. Saez and P. Styring, *Mol. Cryst. Liq. Cryst.* **299**, 163 (1997).
20. G. H. Mehl and J. W. Goodby, *Mol. Cryst. Liq. Cryst.* **303**, 15 (1997).
21. G. Gray, in: *Side Chain Liquid Crystal Polymers*, McArdle, C. B. (ed.), Blackie, Glasgow, 1989.
22. V. Percec and C. Pugh, in: *Side Chain Liquid Crystal Polymers*, McArdle, C. B. (ed.), Blackie, Glasgow, 1989.
23. D. Herren, H. Bürgy and G. Calzaferri, *Helv. Chim. Acta*, **74**, 24 (1991).
24. G. Calzaferri, D. Herren and R. Imhof, *Helv. Chim. Acta*, **74**, 1278 (1991).
25. G. Calzaferri and R. Imhof, *J. Chem. Soc., Dalton Trans.* 3391 (1992).
26. G. Calzaferri, C. Marcolli, R. Imhof and W. Törnroos, *J. Chem. Soc., Dalton Trans.* 3313 (1996).
27. A. R. Bassindale and T. E. Gentle, *J. Mater. Chem.* **3**, 1319 (1993).
28. P. Jutzi, C. Batz and A. Mutluay, *Z. Naturforsch., Teil B* **49**, 1689 (1994).
29. U. Dittmar, B. J. Hendan, U. Flörke and H. C. Marsmann, *J. Organometal. Chem.* **489**, 185 (1995).
30. S. E. Yuchs and K. A. Carrado, *Inorg. Chem.* **35**, 261 (1996).
31. R. Müller, F. Kö and S. Sliwinski, *J. Prakt. Chem.* **9**, 71 (1959).
32. P. A. Agaskar, *Inorg. Chem.* **30**, 2707 (1991).
33. P. A. Agaskar and W. G. Kemplerer, *Inorg. Chim. Acta* **229**, 355 (1995).
34. H. Bürgy and G. Calzaferri, *J. Chromatogr.* **507**, 481 (1990).
35. M. Morán, C. M. Casado, I. Cuadrado and J. Losada, *Organometallics* **12**, 4327 (1993).
36. P. J. Collins and M. Hird, *Introduction to Liquid Crystals* Taylor and Francis, London, 1997.
37. *Handbook of Liquid Crystals* Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W. and Vill, V. (eds), Wiley–VCH, Weinheim, 1998.
38. *Metallomesogens*, Serrano, J. L. (ed.), VCH, Weinheim, 1996, and references therein.
39. H. Ringsdorf and H.-W. Schmidt, *Makromol. Chem. Rapid Commun.* **185**, 1327 (1984).
40. G. Nestor, M. White, G. Gray, D. Lacey and K. Toyne, *Makromol. Chem.* **188**, 2759 (1987).
41. J. L. Speier, *Adv. Organometal Chem.* **17**, 407 (1975).

42. *Comprehensive Handbook on Hydrosilation*, Marciniec B. (ed.), Pergamon Press, Oxford, 1992, and references therein.
43. T. E. Gentle and A. R. Basindale, *J. Inorg. Organometal Polym.* **5**, 281 (1995).
44. M. Ibn Elhaj, A. Skoulios, D. Gouillon, J. Newton, P. Hodge and H. J. Coles, *Liq. Cryst.* **19**, 373 (1995).
45. I. M. Saez, G. H. Mehl, E. Sinn and P. Styring, *J. Organometal Chem.* **551**, 299 (1998).
46. T. J. Bunning and F.-H. Kreuzer, *Trends Polym. Sci.* **3**, 318 (1995), and references therein.