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MONODISPERSE OLIGOMERIC LIQUID CRYSTAL SUPERMOLECULES WITH DEFINED TOPOLOGY

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Abstract This paper describes the synthesis and the characterisation of the phase behaviour of series of siloxane and silsesquioxane based liquid crystals. With increasing the size of the organo-silicone core an increase of the glass and phase transition temperatures occurs. A systematic variation of the branching of the cores and the side-chains yields information about the structure-property relationship of these materials, *e.g.* cores with defined topology are found to exhibit lower glass transition temperatures than comparable cyclic systems.

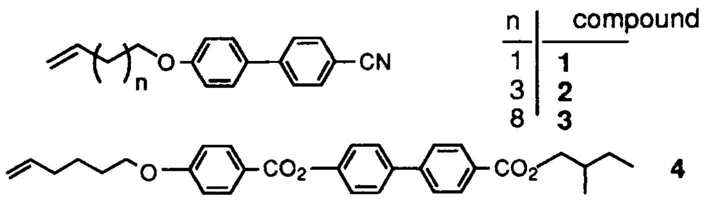
INTRODUCTION

Liquid-crystalline materials, which form a distinct class of supermolecular mesogens, have become interesting subjects of research in recent years because they combine properties of low molar mass liquid crystals *e.g.*, low viscosity with those of polymers, *e.g.* mechanical stability and robustness. However, the physical properties of oligomeric liquid crystals have been found to depend strongly on the degree of polymerisation and dispersity. Consequently, greater interest is now being paid to well-defined discrete molecular systems comprising simple dimers[1], trimers, tetramers[2,3,4]...... to dendrimers. The cores presented in this report, starting from a cross shaped compound **A** *via* prismatic and cuboid cores **B** and **C** to the ring systems **D** and **E** and to a linear material **F** with a DP =35 and $<M_w/M_n>$ of 1.5 were selected in order to allow for some systematic evaluation of the evolution of the phase behaviour with molecular size. To achieve this objective more easily, the structure of the liquid-crystalline side chains was kept intentionally simple.

Experimental

Conveniently, families of liquid crystals of defined size and topology can be prepared *via* a convergent synthetic route which combines a functionalized organo-silicone core with an appropriately substituted olefinic mesogenic unit. In a set of initial experiments a series 4'-ω-alkenyl-4-cyanobiphenyls [4] **1** to **3** were prepared according to published methods and employed as the mesogenic substrates. In order to investigate the influence on the formation and stability of the mesophases of mesogens which favour the formation of tilted phases side chain **4** was reacted with the cores **A** to **F**. A non-chiral material was selected in order to simplify phase identification. The synthesis and the chemical characterisation of the silsesquioxane cores and the final products is described in detail elsewhere[5]. Thermal microscopic studies were made using a Zeiss Universal polarising microscope in conjunction with a Mettler FP52 microfurnace and a FP5 control unit. Calorimetric experiments, relative to an indium standard, were carried out using a Perkin-Elmer DSC 7 calorimeter with a thermal analysis data station. Phase transition temperatures were given as the endothermic onset in the second heating curves (rate: 10 K min^{-1}). Glass transition temperatures were read at the middle of the change in the heat capacity.

RESULTS AND DISCUSSION



n	compound
1	**1**
3	**2**
8	**3**

4

FIGURE 1 Structures of the side-chains.

The targeted products, consisting of the side chains **1** to **4** and the organo-silicones **A** **B**, **C**, **F** were obtained by hydrosylations which were carried out in toluene at room temperature, using Karstedt's catalyst [6]; the cores **D** and **E** were reacted with **4** using Speiers catalyst according to published procedures[7]. These reactions gave complete substitution of all of the Si-H groups present. The replacement of these groups was monitored *via* the disappearance of the Si-H bands in the IR spectra at 2142 cm^{-1} and by the disappearance of the peak at 4.7 ppm in the ^1H-NMR spectrum. The absence of peaks in the vicinity of 2.0 ppm in the ^1H-NMR spectra was indicative (within the experimental error) of complete α-addition of the vinyl groups to the hydrido-silicone moiety. The addition of a small amount of triphenylphosphine was used in these reactions to convert the catalyst to a less reactive platinum triphenylphosphine complex. This technique allowed for a controlled termination of the reaction.

Additionally, upon precipitation into methanol, the platinum triphenylphosphine complex remained in solution which allowed for the easy isolation of products. Consequently, the final products were not coloured by platinum residues. The values for the transition temperatures, and the associated enthalpies for the second heating cycles for compounds **5** to **10** are listed in Table 1.

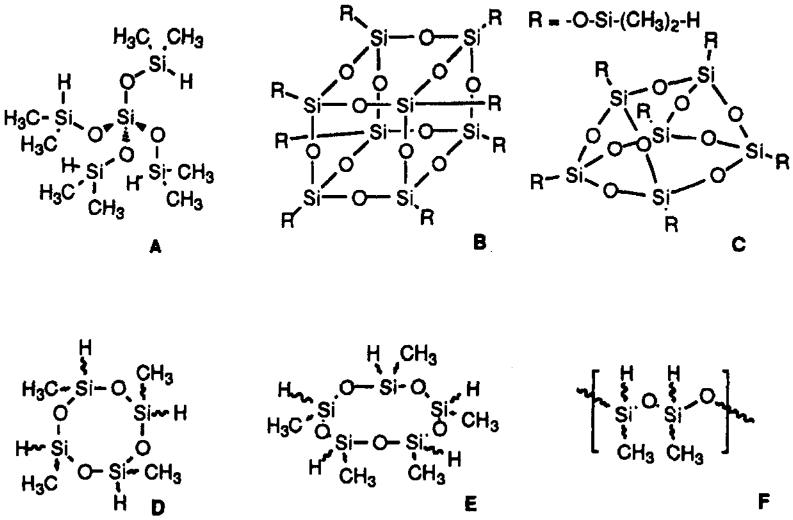


FIGURE 2 Structure of the organo-silicone cores.

Thermal polarised light transmission microscopy reveals for the materials **5** to **10** the formation of a focal-conic defect texture, with hyperbolic and elliptical lines of optical discontinuity being formed, 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. For compound **9**, below 44 °C the formation of a broken focal conic texture[4] indicative of the formation of a smectic C phase is formed. For materials **5**, **6** and **7**, deriving from core **A**, the glass transition temperature varies from -14.7 to -6.3 °C, for compounds **8**, **9** and **10** stemming from core **B** a decrease of the glass transition temperature with increasing spacer length was observed. For both cores the clearing temperatures increase with lengthening the spacer. A remarkable feature of these systems is that, whereas the clearing temperatures are more or less similar, the glass transitions differ considerably. The injection of a higher ordered smectic phase close to the glass transition in compound

7, and the occurrence of soft crystal phases and crystal phases in **9** and **10**, indicates a strong increase of ordering of the molecules with increasing spacer length. A comparison of systems having four and eight branches indicates that the latter tend to exhibit a richer crystalline morphology. This observation is supported by an increase of the values transition enthalpies with ascending the series. On a molecular level this could be explained by the increasing separation of the mesogenic cyanobiphenyl groups from the core. Due to the reduced steric hindrance with increasing spacer length stronger intramolecular interactions between the mesogenic groups seem to be favoured.

TABLE 1 Transition and glass transition temperatures (°C), specific heats ΔCp (J g^{-1} K^{-1}) and transition enthalpies (J g^{-1}) as determined by DSC measurements (10°C min^{-1}); [a] Cpd = compound, [b] Sdch = side chain, [c] n = spacer length, [d] S_W, S_Y, S_X, S_Z are yet unresolved crystal or soft crystal phases, [e] observed by microscopy.

Cpd [a]	Sdch[b]	Core	n [c]	T_g	Phase transitions
5	1	A	4	-9.6 [0.34]	S_A 88.7 Iso [4.85]
6	2	A	6	-14.7 [0.36]	S_A 118.7 Iso [7.83]
7	3	A	11	-6.3 [0.31]	S_W[d] 38.7 S_C[e] 44.0 S_A129.7 Iso [18.2] [-] [12.34]
8	1	B	4	11.0 [0.22]	S_A 93.9 Iso [4.31]
9	2	B	6	3.0 [0.32]	S_X[d] 22.5 S_A 116.5 Iso [0.19] [5.40]
10	3	B	11	-7.5 [0.28]	cr 34.4 S_Y[d] 54.6 S_Z[d] 64.5 S_A 128.5 Iso [10.2] [0.77] [1.20] [8.66]

For the materials derived from the side chain **4**, whose structure promotes the formation of tilted phases the results are listed in Table 2. For the description and understanding of the phase behaviour of these materials their essentially trichotomous molecular structure has to be taken into consideration. If smectic phases are to be formed, the mesogens of these materials are part of two adjacent layers, linked together by the organo-silicone group. The type and stability of the liquid-crystalline phase will therefore be determined by the structure of the mesogenic side chains and the structure of the organo-silicone core. The core influences via its geometry, the concentration of stereo isomers, its tendency to phase separate and *via* the amount of branches the phase behaviour considerably.

For cyclic liquid-crystalline materials made of small rings consisting of different isomers in order to fit to structures of smectic phases they have to be inscribed into a cylindrical (spindle) shaped structure, with the smallest radius in the core, *i.e.* the area of the siloxanes, and the largest at the terminal groups of the molecule. Due to the limited amount of mesogens per core, one molecule cannot fill the cylindrical envelope, which has to be filled by intermolecular interaction

Low Tg's and low viscosity can in this model be explained as result of the flexibility of the core and gaps in the cylinder[2,3]. Increasing the diameter of the core from four **12** to five **13** silicones leads to an increase of the number of gaps. The glass transition temperature is not much affected by this increase in disorder, the transition temperatures of the mesophases however decreases and a highly ordered phase present (S_X) is lost altogether.

TABLE 2 Transition and glass transition temperatures (°C), specific heats ΔCp (J g^{-1} K^{-1}) and transition enthalpies (J g^{-1}) as determined by DSC measurements (10°C min^{-1}); [a] Cpd = compound, [b] S_X is a yet unresolved phase, * unresolvable by DSC.

Cpd [a]	Core	Tg	Phase transitions
4	Monomer	-	cr 78.5 S_C 106.1 S_A 157.2 N 168.9 Iso [0.68] [2.93] [1.51]
11	A	-8.4 [0.47]	S_{Ca} 125.0 S_C 154.4 S_A 164.4 Iso [0.13] [0. 1] [-]*
12	D	10.3 [0.54]	S_X[b] 69.5 S_C 184.2 N 193.3 Iso [1.03] [-]* [8.0]
13	E	11.2 [0.37]	S_C 182.5 S_A 188.7 Iso [-] [6.82]
14	C	11.5 [0.14]	S_C 191.5 Iso [2.1]
15	B	-	cr 143.0 S_C 208.0 S_A 214.0 Iso [21.1] [0. 2] [6.4]
16	F	19.0 [0.15]	S_C 223.5 S_A 234.3 Iso [0. 1] [5.33]

The use of hexasilsesquioxane **C** or octasilsesquioxane **B** cores leading to materials **14** and **15**, where the gaps in the cylinder are filled, leads to an increase in the mesophase stability resulting in values not much lower than in a much larger linear polymer **16**. The rigidity of the cores tends to increase the melting temperatures of the materials. The question why the prismatic system does not crystallise could be rationalised *via* the more marked influence of the dimethylsiloxane groups next to the core in this system. More detailed investigations of these systems are however necessary to understand the properties of these and related materials.

The compound **11** with the tetrahedral **A** core has a markedly different phase behaviour from the other materials, which can be rationalised in the following manner. Due to its crowded central core with its eight methyl groups the glass transition and clearing temperature are much lower than in all the other materials. Thus it is possible that because of the intramolecular interactions facilitated through the close proximity of the side-chains, similar liquid-crystalline phases can be realised as found for the other materials. Additionally a S_{Ca} phase identified *via* its transition enthalpy and the occurrence of two and four brush defects in its *schlieren* texture occurs, which could not be observed in the other materials.

CONCLUSION

The phase behaviour of materials derived from combination of mesogenic side chains with organo-silicone series cores shows that liquid-crystalline phase behaviour occurs. Depending on the core and the side chains selected, the glass transition and clearing temperatures can be widely varied. By keeping the mesogenic unit constant and increasing the spacer length the formation higher ordered crystal or soft crystal phases is promoted. A comparison of a series of organo-silicone cores reacted with a side chain promoting the formation of tilted liquid crystal phases shows that generally speaking with increasing the number of side-chains the transition temperatures increase. The use of suitably selected cores tends to promote the formation of liquid-crystalline phases not present in the monomeric side chain or the linear polymer.

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