Substituted siloxysilanes and the structure of oligomeric liquid crystals

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The sequential addition of 4-cyanobiphenyl moieties to a silyl core unit results in a modification of the molecular shape of the molecules from rod-like to cross-shaped. The variation of molecular size and shape determines the nature (interdigitated SmAd or monolayer SmAl) and the stability range of the liquid-crystalline phases of these materials.

The research into branched and hyper-branched systems has focused mainly on synthesis of 'number generation' and less attention has been paid to the influence of the sequential introduction of sub-molecular systems into supermolecular structures.[1,2]

In order to understand this influence it is necessary to investigate the properties of the submolecular blocks and to examine how the stepwise introduction of those units into each generation of the supramolecular scaffolding affects the properties of the system.

This allows for the examination of the relationships and interplay between discrete molecular and polymeric systems and between the submolecular units, the polymeric framework, and the topology of their interconnections.

The above relationships are of importance to low molar mass, oligomeric and polymeric liquid-crystalline systems where there is constant debate concerning the identities, dynamics and topologies of mesogenic groups, spacer chains and polymer backbones in complex macromolecular systems. These relationships are of particular importance in determining viscoelastic and rheological properties. For example, it has been shown that defined or discrete oligomeric materials can exhibit properties usually associated with polymers, whilst still retaining the fluidity and viscosity of low molar mass liquid crystals.

In order to investigate these relationshps a series of model materials was synthesised, consisting of molecules where the number of mesogenic groups attached to a central silane core was sequentially increased in number from one to four. In addition the associated solid state behaviour of each of the materials was investigated. In this systematic study we prepared and investigated a family of branched supermolecules that were designed to have a controllable number of 4-cyanobiphenyl mesogenic submolecular units attached to a central silane core. The materials were conveniently prepared *via* a synthetic route based on combining a 4'-ω-alkenyl-4-cyanobiphenyl with an (oligo)vinylsilane moiety.

Initially, 4'-(10-undecenyl)-4-cyanobiphenyl was treated with a tenfold excess of 1,3-dihydro-1,1,3,3-tetramethylsiloxane in a hydrosylation reaction that was carried out in toluene at room temperature using Karstedt's catalyst (Pt–divinyl-tetramethylsiloxane in xylene), thereby yielding [4-cyano-4′-{11-[3-hydro-1,1,3,3-tetramethyldisiloxy]undecanyloxy}biphenyl] **1**.[3–5] The target materials **2–5** were obtained under similar reaction conditions, but by using an excess of **1** relative to the number of reactive vinyl groups in the silane cores (alkylvinylsilanes) to which the mesogenic submolecular units were to be attached. In each case, isolation of the product (**2–5**, Fig. 1) was achieved by column chromatography over silica gel using a mixture of hexane–dichloromethane (6 : 1) as the eluent. The absence of peaks in the vicinity of 2.0 ppm in the ^{1}H NMR spectra was indicative (within experimental error) of complete α-addition of the vinyl groups to the hydridosilicone core unit. The ^{29}Si NMR spectra revealed the shift of the signal of the hydridosiloxane group at 10.0 ppm to values of 7.08 to 7.43 ppm after conversion (the exact value measured being somewhat dependent on the structure of the core). The signal for the silicon bonded to four alkyl groups was found to shift from 3.04 to 6.88 ppm with the concomitant increase in the number of mesogenic substituents from one to four. These results were matched by high resolution ^{1}H NMR spectra, which is not usually the case for oligomeric materials.

Calorimetric studies reveal that all of the materials exhibit liquid crystal phases. 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 polarised light transmission microscopy reveals that as each material is cooled from the isotropic liquid into the liquid crystal state, homeotropic and focal-conic defect textures are formed. The combination of homeotropy with the hyperbolic and elliptical lines of optical discontinuity associated with focal-

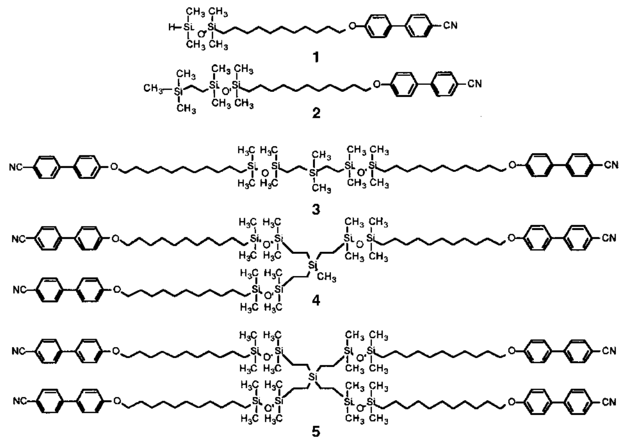

Fig. 1 Structure of the liquid-crystalline materials **1**–**5**.

Table 1 The transition temperatures (°C) and enthalpy and entropy data (ΔH/J g^{-1}, ΔC_p/J g^{-1} K^{-1}) obtained for compounds **2**–**4**. Cr$_1$, Cr$_2$, Cr$_3$ and Cr$_4$ are crystal or soft crystal phases.

Compound	T_g/°C (ΔC_p/J g^{-1} K^{-1})	Transition temperature/°C and enthalpies (ΔH/J g^{-1})	$\Delta S_{mol}/R$	$(\Delta S_{mol}R)/n$
2	—	Cr 27.3 (57.6) SmA 50.6 (4.14) Iso Liq	0.90	0.90
3	—	Cr 30.8 (30.89) SmA 76.0 (7.53) Iso Liq	2.79	1.40
4	−28.5 (0.19)	Cr$_1$ − 19.6 (−6.51) Cr$_2$ 20.3 (4.25) Cr$_3$ 22.4 (−2.58) Cr$_4$ 35.0 (14.54) SmA 89.1 (4.89) Iso Liq	2.55	0.85
5	−22.3 (0.42)	Cr$_1$ −10.2 (−13.05) Cr$_2$ 27.2 (10.17) Cr$_3$ 29.2 (−12.48) Cr$_4$ 50.8 (27.48) SmA 97.9 (7.77) Iso Liq	5.20	1.30

conic defects is diagnostic for the presence of a smectic A phase. Mechanical shearing of the specimens in the microscope shows that the smectic A phase flows easily and has a relatively low viscosity. In addition, only a short time is required for the focal-conic defect pattern to form on cooling from the isotropic liquid, indicating that the compounds have rheological properties more in common with low molar mass materials than with oligomers or polymers.

Increasing the number of branches carrying mesogenic groups from one to four results in the isotropization temperature being increased from 50.6 °C for compound **2** to 97.9 °C for **5** indicating an increasing stability of the liquid crystal properties as a function of the number of mesogenic units. Interestingly, if the values of the reduced molar entropy ($\Delta S_{\mathrm{mol}}/R$) are used as a measure of the degree of ordering within the liquid crystal phase at the isotropization temperature an alternating odd–even effect is manifested. The middle members, **3** and **4**, exhibit roughly similar values of 2.79 and 2.55 placing them between those of the terminal members of the series, *i.e.* 0.90 for **2** and 5.20 for **5**. Taking into account the number of mesogenic moieties per molecule [$(\Delta S_{\mathrm{mol}}/R)/n$] reveals an odd–even effect. The odd members of the series have reduced molar entropies between 0.8 and 0.9, and the even substituted materials have values between 1.3 and 1.4 per mesogenic side-chain. This result is in line with the concept of having a higher degree of ordering in the liquid-crystalline state for the even members of the series. This can be attributed to the higher degree of molecular symmetry of the even members. The higher degree of symmetry helps in the intra- and inter-molecular packing of the mesogenic subunits or arms, which in turn aids the organization and packing of the supermolecules within the layers of the smectic phase. Moreover, the occurrence of glass transitions for materials **4** and **5**, with an increase in their vitrification temperatures from −28.6 to −22.3 °C as the series is ascended, suggests that there is a higher degree of polymeric character associated with the materials as the number of mesogenic units is increased.

The structure of the smectic A phase exhibited by the materials was investigated further using X-ray diffraction. High flux synchrotron radiation was used in order to perform temperature scans at a rate of 2 °C min^{-1} for fibre samples in Lindemann tubes. The diffraction patterns were found to be typical of the smectic A phase. The results for the *d*-spacings (*d*) for compounds **2**–**5**, as a function of the reduced temperature ($T - T_{\mathrm{iso}}$) from the isotropization point (T_{iso}), are shown in Fig. 2. For all of the materials a reduction in the *d*-spacing was observed as the isotropization point was approached. The members with a higher degree of substitution were found to have smaller *d*-spacing than the mono- or di-substituted materials. These results agree with earlier findings for other liquid-crystalline oligosiloxanes.[5–7]

The comparison of the calculated lengths (*l*) of the simulated structures of **2**–**5** (Cerius^2, 3.0 from MSI) with the corresponding layer spacing (*d*) gives *d*/*l* values of 1.6 for **2** and between 0.9 and 1.0 for compounds **3**–**5**, Table 2. The result for compound **2** fits with an interdigitated bilayer structure for the smectic A phase, thereby classifying the phase as smectic A_d. Interdigitation takes place *via* overlap of the aromatic regions of the dimeric molecules in adjacent lamellae. The decrease in the *d*-spacing with rising temperature for compounds **2** can then be attributed either to increased disordering of the molecules or increased overlap of the molecules. The *d*/*l* values of 0.9–1.0 for the higher homologues indicate the occurrence of a different phase structure for the smectic A phase. One possibility is that the supermolecules in their fully extended conformational structures are arranged in disordered monolayers as in a conventional smectic A_1 phase. As each molecule possesses silyl and aromatic moieties, when these molecular subunits pack together they can do so *via* internal microphase separation. Thus for a microphase separated structure an object molecule can provide mesogenic units to potential aromatic layers above and below a layer containing the silyl core units. Thus, the results are consistent with a structure where the silicone cores are located in the central regions of the layers and where some overlap of the terminal cyanobiphenyl groups occurs between layers.[5,6] This classifies the high temperture smectic phase for the materials **3**–**5** as smectic A with respect to the silane core and quasi-smectic A bilayer for the mesogenic units.

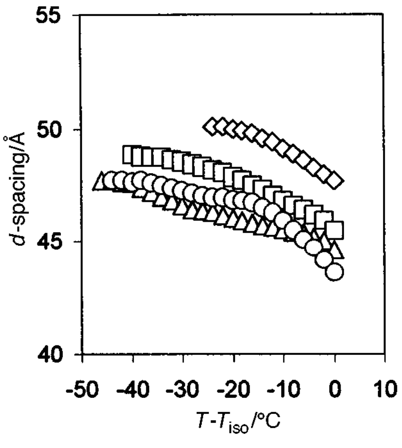

Fig. 2 *d*-Spacings for compounds **2**–**5** plotted against the reduced temperature $T_{\mathrm{Iso}} - T$; (◇) **2**, (□) **3**, (△) **4**, (○) **5**.

Table 2 *d*-Spacings determined by X-ray diffracton and calculated lengths for compounds **2**–**5**

Compound	Calc. length *l*/Å	$d_{\max}/l$	*d*-Spacing (max)/Å	*d*-Spacing ($T_{\mathrm{Iso-10}}$)/Å
2	30.8	1.63	50.1	48.8
3	48.4	0.98	48.8	46.6
4	49.6	0.96	47.7	45.6
5	50.9	0.94	47.7	45.6

For this series the results indicate that as the number of mesogenic groups is increased the temperature range of the liquid crystal state increases. The ordering of the molecules within the structure of the mesophase tends to be higher for the members of the series that have an even number of mesogenic subunits attached to the central silicon atom. This may be due to symmetry considerations allowing for better packing of the molecules. As the mesogenic count per silyl core is increased so the mesogenic arms have less freedom of movement, and therefore certain molecular topologies become favoured, this in turn affects the physico-chemical properties.

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