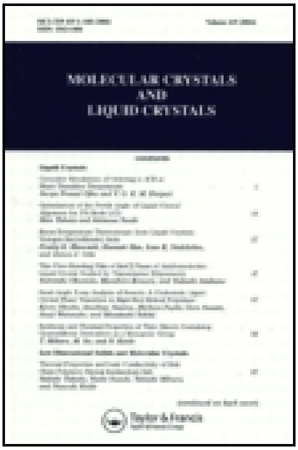

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Oligomers and Dendrimers Based on Siloxane and Silsesquioxane Cores: Does the Structure of the Central Core Affect the Liquid-Crystalline Properties?

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A series of oligomeric and first generation dendritic materials based on silane-siloxane and silsesquioxane core has been synthesised. The attachment of cyano-biphenyl mesogens separated by spacers to these cores which were varied systematically, resulted in liquid-crystalline materials. The synthesis of the materials is outlined and the liquid-crystalline phase behaviour of the materials, which are of uniform in size and stereochemistry, is described.

Keywords: Dendrimers; Liquid Crystal; Silsesquioxane; Silane-Siloxane; Oligomer

For supra-molecular materials which are related to calamitic low molar mass liquid crystals a number of structural elements determine the mesophase behaviour. These are the degree of polymerisation, the polydispersity and the stereo-chemical structure of the molecular scaffold [1-4].

In order to investigate the influence of these elements on the liquid-crystalline phase behaviour of materials which contain cyano-biphenyl mesogens, a series of compounds was synthesised.

The materials whose structure contains a spacer consisting of eleven methylene groups and tetramethyldisiloxane group are depicted in Figure 1. This spacer configuration was selected in order to gain a large degree of decoupling between the mesogen and the central core. A silane group was selected as a central core. This allowed for the systematic substitution of methyl groups bonded to the silane core with ethylene groups. These make up the linkage with the siloxane end-groups of the side-chains.

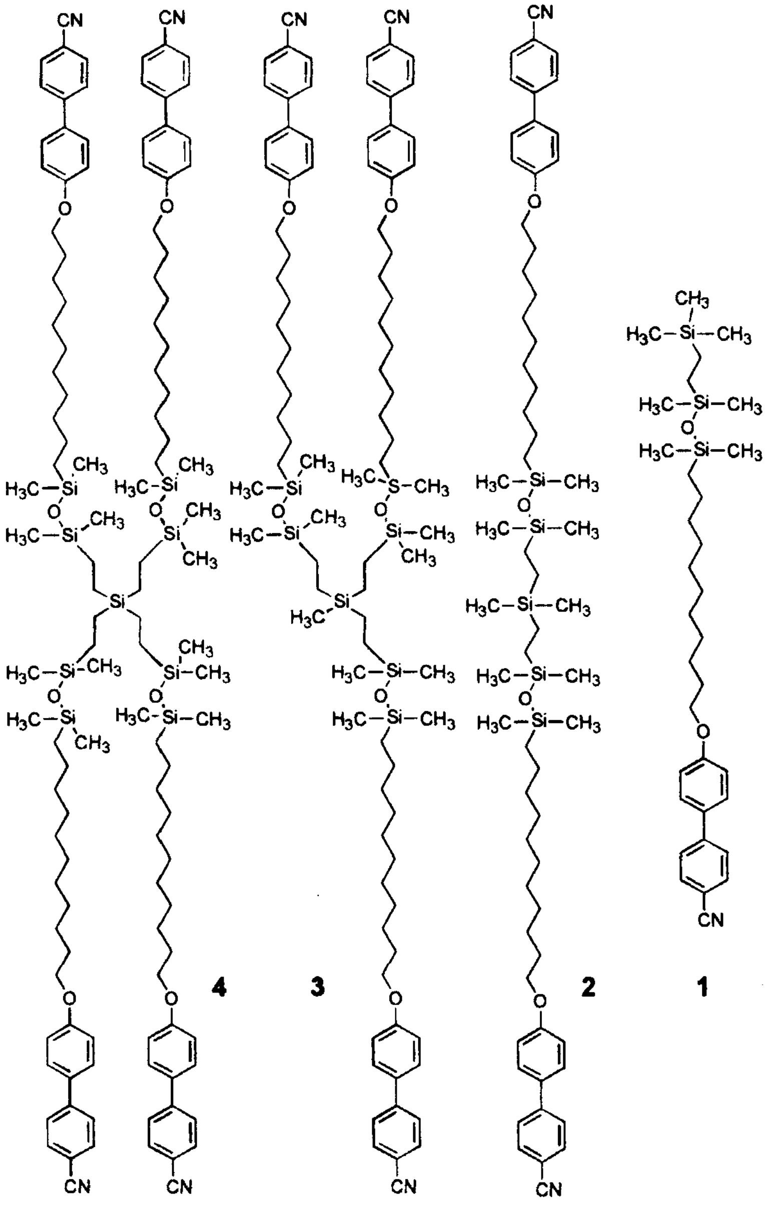

FIGURE 1: Chemical structures of the materials **1**, **2**, **3** and **4**.

This approach allowed for the synthesis of materials which are monodisperse and oligomeric with respect to the number of side-chains per molecule. Additionally the structure of the central core provides for the lack of stereo-isomers.

The liquid-crystalline properties, which were determined using DSC and optical polarising light microscopy are listed in Table 1. The liquid-crystalline phase preceding the isotropisation temperature was identified as smectic A.

Compd	T_g (°C) [ΔCp (J g^{-1} K^{-1})]	Transition Temperatures (°C) and enthalpies [ΔH (J g^{-1})]
1	-	Cr 27.3 [57.6] SmA 50.6 [4.14] Iso Liq
2	-	Cr 30.8[30.89]SmA 76.0 [7.53] Iso Liq
3	-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
4	-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

TABLE 1: The transition temperatures (°C) and enthalpy and entropy data [ΔH (J g^{-1}), ΔCp (J g^{-1} K^{-1})] obtained for compounds **2** to **4**. Cr_1, Cr_2, Cr_3 and Cr_4 are crystal or soft crystal phases.

The isotropisation temperature for the materials increased from 50.6 °C for **1** to 97.9 °C for **4**. The materials **2** and **3** with two and three side-chains exhibit isotropisation temperatures of 76.0 and 89.1 °C. For the materials **3** and **4** relatively low glass transition temperatures of -28.5 for **3** and –22.5 °C for **4** could be observed. An interesting feature is that all of the materials of this series exhibit crystalline phases. The number of crystalline phases and the stability range of the crystal state increases with increasing the number of side-chains.

The crystal state for compound **1** is stable up to 27.3 °C for material **4** four crystalline phases separated by melting and recrystallisation processes could be observed. Material **4** melts from its highest stable crystalline state at 57.3 °C into a smectic A phase.

For the series it was detected that the range of the liquid-crystalline state increases with increasing the number of mesogens per molecule, as shown in Figure 2.

The phase structure of the materials in the stability range of the smectic A phase was investigated using X-ray diffraction, described in more detail elsewhere [5].

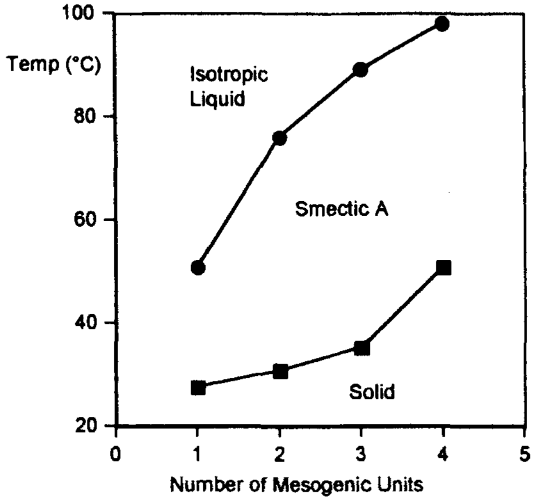

FIGURE 2: The transition temperatures for the compounds **1** to **4**.

For the materials **1** to **4** with increasing temperature a decrease of the smectic layer spacing listed in Table 2 was detected. The largest layer spacings were found close to the melting point from the crystal phase. The observed values of 47.7 to 48.8 Å for materials **2** to **4** correlate well with the estimated molecular lengths of the molecules in their fully extended conformations. The estimations of the molecular lengths were obtained using Cerius^2 molecular modelling software from MSI in a manner described in more detail elsewhere [6].

The results indicate that the smectic A phase of the materials **2** to **4** is a conventional smectic A phase. For material **1** a value of the layer spacing of d = 50.1 Å is considerably larger than the estimated length of the molecular structure of 30.8 Å. The value d/L of 1.6 correspond well for the values expected for an interdigitated bilayer smectic A phase.

Compound	Calc. Length l (Å)	D_{max}/l	d-spacings (max) (Å)
1	30.8	1.63	50.1
2	48.4	0.98	48.8
3	49.6	0.96	47.7
5	50.9	0.94	47.7

Table 2: The d-spacings (Å) by X-ray diffraction and calculated lengths (Calc Length) l for compounds **1** to **4**.

In order to explore the question of the effect of an increase of the number of mesogenic groups per central core the structure of the core and that of the mesogens were varied. The side-chains **5** and **6** whose synthesis is described elsewhere were coupled to the cores **A** and **B** [7]. They are depicted in Figure 3. The decoupling of the core and the mesogenic groups is achieved by increasing the length of the spacer for **5**. Branching by using a malonate group allowed for the synthesis of material **6** which contains two mesogenic groups per branch point.

The products **7** and **8** were synthesised in order to monitor the influence of siloxane moiety on the phase behaviour of the compounds **5** and **6**. The fusion of **5** and **6** to the pentamethyl-siloxane core group **A** was achieved via hydrosylilation reactions. The attachment to core **B** lead to materials **9** and **10**. Compound **10** is a first generation dendrimer with defined size and stereo-chemistry. The liquid-crystalline phase behaviour of the materials is listed in Table 3.

Compd	Structure	Transition Temperatures (°C) And enthalpies [ΔH (J g^{-1})]
5	monomer	Cr 58.8 (SmA 43.5 [9.1]) Iso Liq
6	monomer	Cr 65.8 (SmA 63.6 [7.9]) Iso Liq
7	A + 5	Cr 53.4 (SmC 42.1 [11.7]) Iso Liq
8	A + 6	Cr 45.1 SmA 71.4 [11.7] Iso Liq
9	B + 5	Cr 34.5 SmX 44.2 SmC 64.2 [10.3] Iso Liq
10	B + 6	Cr 35.1 (SmC 29.8) SmA 95.7 [9.2] Iso Liq

TABLE 3: The transition temperatures (°C) and enthalpy data [ΔH (J g^{-1})] obtained for compounds **5** to**10**. Cr, and SmX are crystal and unidentified smectic phases.

Materials **5** and **6** exhibit both a monotropically stable smectic A phase. The attachment to the core **A** changes the liquid-crystalline phase type and stability. For the linear material **7** a monotropic smectic C phase was observed. It is stable up to 42.1 °C. The branched material **8** exhibits an enantiotropic smectic A phase up to 71.4 °C. This is an increase of the liquid-crystalline phase range by 7.8 °C compared to the monomer **6**.

The fusion to the silsesquioxane core **B** lead to materials **9** and **10**. Compound **9**, the material with the linear side–chains exhibits an enantiotropic smectic C phase with a clearing temperature of 64.2 °C. The melting point is depressed to 34.5 °C compared to 58.8 °C for **5**. Additionally a second smectic or soft crystal phase (smectic X) occurs below 44.2 °C. For the branched mesogen **6** the attachment to the core **B** leads to a liquid-crystalline dendrimer.

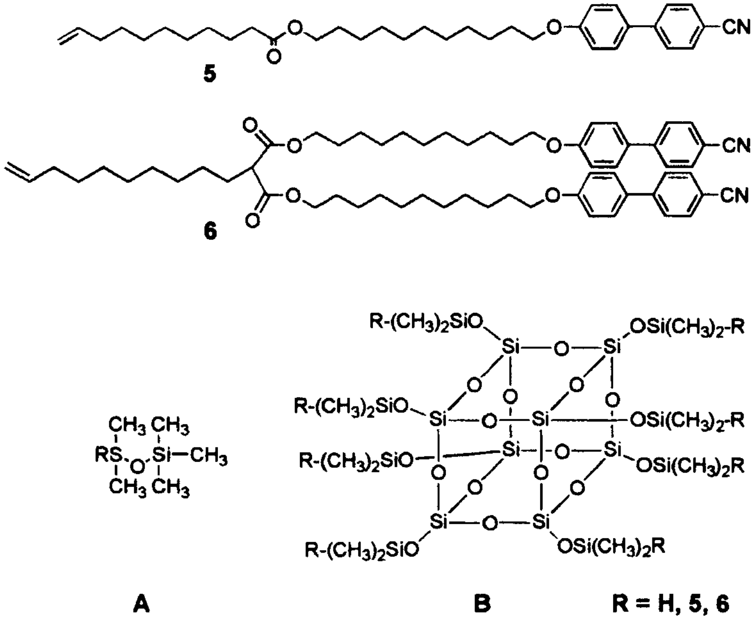

FIGURE 3: Chemical structures of the compounds 5 and 6 and of the siloxane core A and the silsesquioxane core B (R = H).

For this material the stability range of the smectic A phase is enhanced up to 95.7 °C. Additionally the formation of a monotropic smectic C phase preceding crystallisation was observed.

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