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Preliminary communication

Supermolecular liquid crystal dendrimers based on the octasilsesquioxane core

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Liquid crystalline dendrimers are proving to be a fascinating class of materials that possess unusual physical properties. The self-assembling process involved in the formation of the mesomorphic state apparently deforms the spherical disposition of the supermolecular dendrimers to give rod-like entities that pack together to yield disordered Smectic A and smectic C mesophases.

Investigations into branched and hyperbranched supermolecular systems, such as star-shaped dendrimers, have led to the establishment of a new field of materials research [1, 2]. The stepwise synthesis of new supermolecular systems generally results in the creation of monodisperse materials that have beautifully symmetrical molecular structures. The process of growing hyperbranched systems by increasing the number of generations of the sub-molecular building blocks typically leads to supermolecular systems that have complex molecular structures, higher levels of symmetry, and unusual physico–chemical properties. However, the supermolecular architecture changes as the density of the sub-molecular building blocks in each generation is increased, and as the density rises so the molecular shape tends towards becoming globular or spherical. As a consequence, it is intriguing to examine how the molecular geometry of a supermolecular system is altered, constrained and deformed by being placed in an alien environment where the system does not have total dynamical freedom. In this article we investigate the effects that a self-organizing fluid system, such as the environment found in a liquid crystal mesophase, has on the topology and shape of a supermolecular material that is disposed to being spherical in the gas phase.

Octasilsesquioxane provides a useful central core system for such studies because it has potentially eight points where it can be derivatized with mesogenic moieties, and also there is the potential for doubling or tripling the number of mesogenic units [3]. In an earlier study eight cyanobiphenyl moieties were attached to the octasilsesquioxane core by way of flexible aliphatic chains [4], see figure 1. It was found that the resulting supermolecular materials, where the flexible aliphatic spacer chain was varied in length, exhibited lamellar smectic A phases. This result indicated that the mesogenic units must associate with one another, thereby changing the globular shape of the molecular structure into a rod-like form. X-ray diffraction studies showed that the rod-like supermolecules packed in disordered layers. Thus, it appeared that the fluid-like liquid crystal environment was affecting the topology of the supermolecules. Molecular simulations suggested that the density of the mesogenic units was such that they could pack in groups of four on either side of the octasilsesquioxane core thereby giving a cylindrical molecular shape. Thus this particular molecular architecture could be thought of as giving a closely packed, high density system.

In this present study the number of mesogenic groups surrounding the octasilsesquioxane core was doubled in number to sixteen, thereby forcing the supermolecular architecture to be more globular/spherical in shape, see structure **1**. By doubling the number of mesogenic groups it was expected that a competition would be created between the need for the molecular shape to remain spherical because of packing constraints and the ability of the supermolecular system to be deformed to fit in with its mesomorphic environment. By increasing the density of mesogenic moieties, we expected to breach the boundary for the transformation from the lamellar to cubic or columnar phases. Such a result would demonstrate that thermotropic mesophases are affected by molecular curvature in exactly the same way that

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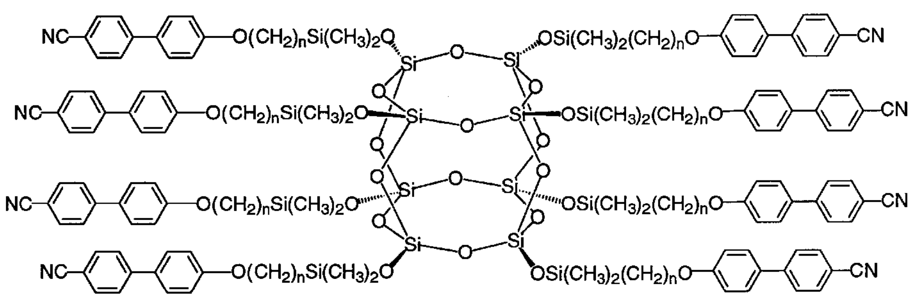
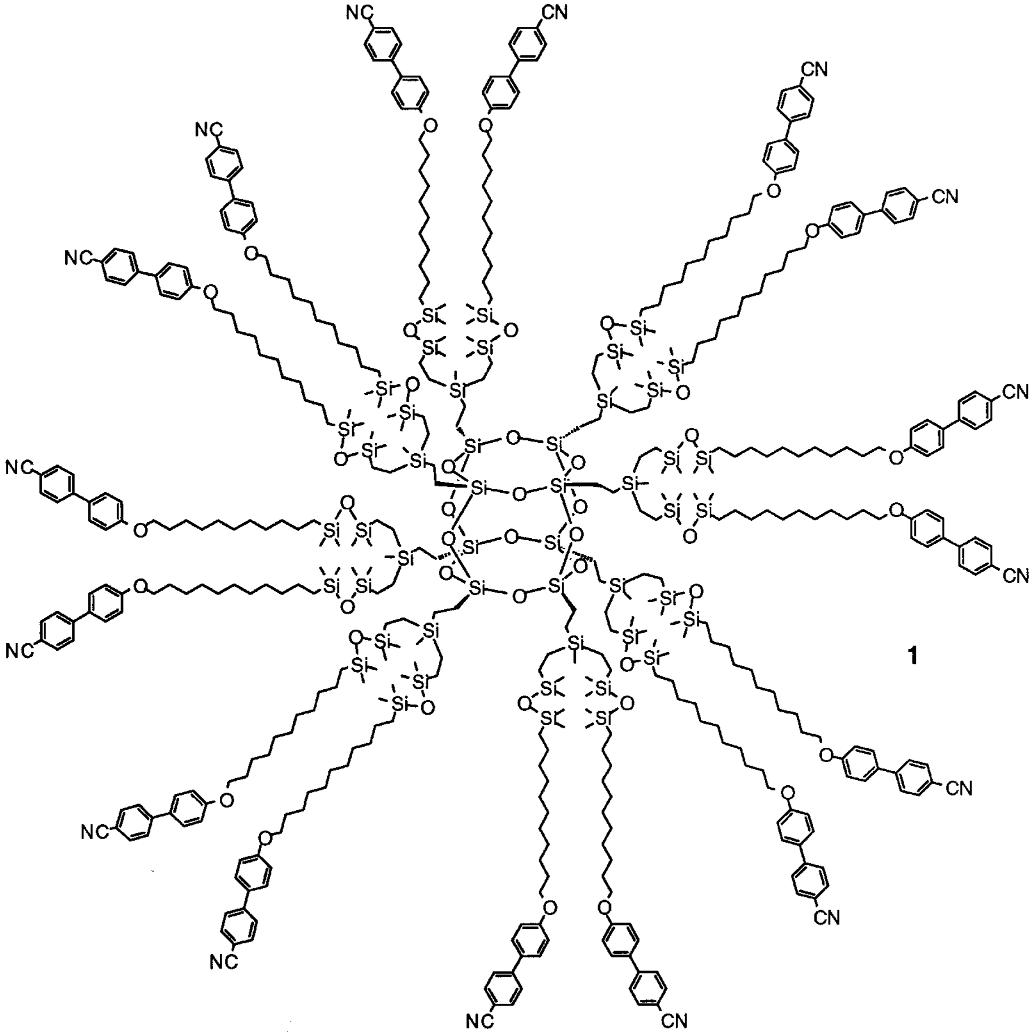


n	Tg		SmA		I
4	•	11.0	•	93.9	•
6	•	0.3	•	116.5	•
11	•	-7.0	•	128.5	•

Figure 1. Phase transition temperatures (°C) for octasilsesquioxane core with eight attached cyanobiphenyl moieties.



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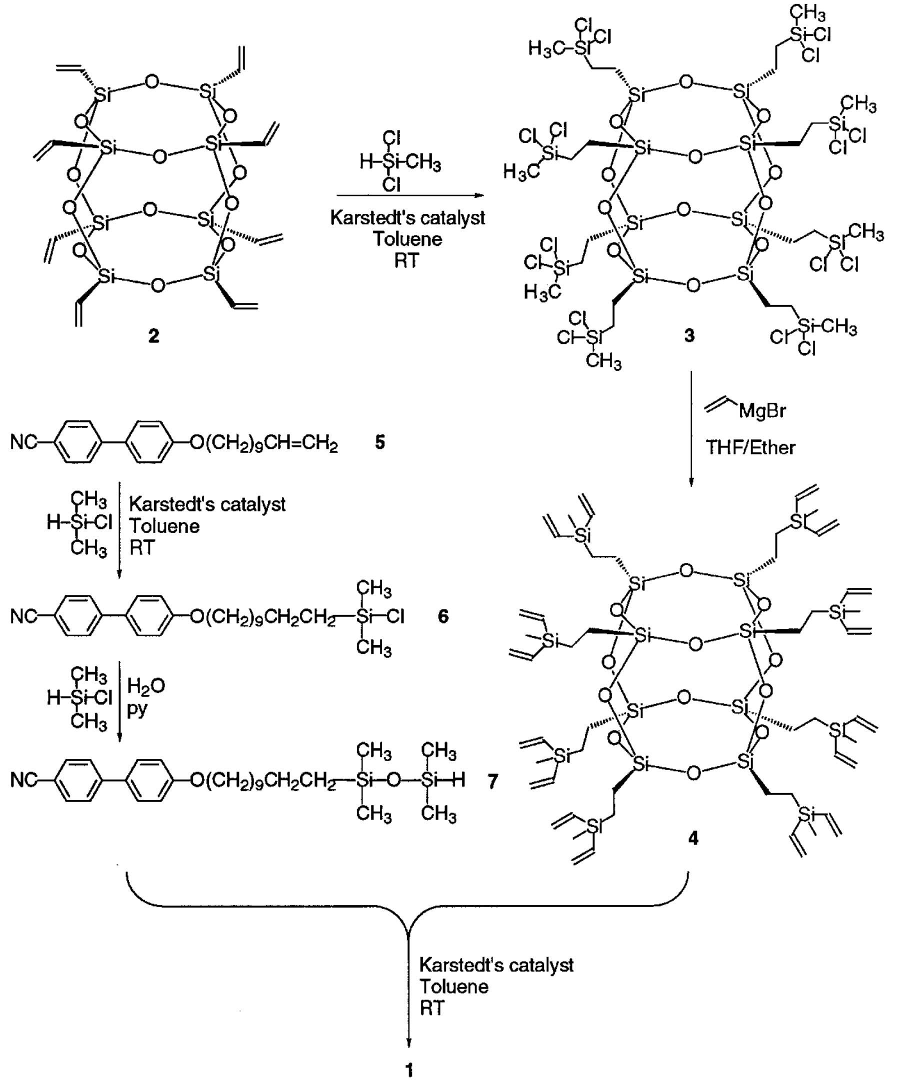
Structure 1.

curvature affects lyotropic systems. Thus the mesomorphic properties of the synthesized dendrimer **1** were investigated, and remarkably the results show that even for a more densely packed system the mesomorphic environment is strong enough to deform the molecular topology in order to support lamellar mesophases.

The octasilsesquioxane core was synthesized, see the scheme, starting from octavinyloctasilsesquioxane **2**, via an alkenylation/hydrosilylation sequence, to afford the first generation dendrimer **4**, which possesses 16 vinyl groups. Hydrosilylation of **2** with $HSiMeCl_2$, using Karstedt's catalyst [5] affords **3**; compound **3** was treated, without further purification, with an excess of vinyl magnesium bromide to give **4** in 30% isolated yield. Compound **4** was characterized by conventional spectroscopic methods, elemental analysis and MALDI-TOF spectrometry. Of particular diagnostic value was ^{29}Si NMR spectroscopy, which indicated by symmetry that the core was completely functionalized, and that the silsesquioxane cage had remained intact during the steps for dendritic growth. MALDI-TOF spectroscopy gave the correct molecular weight for $(M+Ag)^+$. GPC ascertained that the product was monodisperse, but underestimated the value of its molecular weight due to the globular conformation of the molecular structure; this is usually the case for dendrimers.

The synthesis of the mesogenic substrate [6] was achieved by firstly hydrosilylating 4′-(11-undecenyloxy)-4-cyanobiphenyl, **5**, with dimethylchlorosilane to give compound **6**. The co-hydrolysis of **6**, with an excess of dimethylchlorosilane in water, using pyridine as a base, afforded compound **7** in high yield, as the only cyanobiphenyl species; this was easily isolated and purified by column chromatography. Compound **7** showed expected features in the ^1H NMR spectrum, notably a septet at 4.65 ppm due to the Si–H resonance, and the exclusive



Scheme.

formation of the β-isomer from the addition of the Si–H bond to the terminal alkene. ^{29}Si NMR spectroscopy confirmed the presence of two M-type silicon atoms in slightly different environments, at 10.00 ppm (O–*Si*–CH$_2$) and – 6.81 ppm (O–*Si*–H).

Hydrosilylation of the vinyl groups of the G$_1$-vinyl silsesquioxane dendrimer with a slight excess of **7** catalysed by 'Pt' was carried out at room temperature. The progress of the reaction was monitored by FTIR and TLC. The reaction proceeded rapidly at room temperature, but was allowed to run for three days to ensure complete conversion. When the reaction was judged to be complete, a few crystals of PPh$_3$ were added to deactivate the catalyst and to allow a controlled termination of the reaction [4]. Dendrimer **1** was isolated by repeated precipitation in methanol, in 54% yield.

^{1}H NMR spectroscopy of dendrimer **1** shows all of the expected features, with well resolved signals for the cyanobiphenyl moieties indicating full conformational freedom in solution for the sixteen mesogenic fragments. This result indicates that the mesogenic moieties are in surroundings that are more akin to a monomeric than a polymeric environment. The Si–*CH*$_2$ pseudo-triplets are overlapped, as the CH$_2$ groups are placed now in very similar environments; this makes it difficult to differentiate between the internal (generation 0) and the external (generation 1) Si–CH$_2$–CH$_2$ segments of the dendritic arms. However, the presence of a small number of residual unreacted vinyl sites could be detected, indicating some incomplete conversion. Integration of the signals at ~5.60 ppm revealed a coverage of 14 ± 2 mesogens per molecule.

^{13}C NMR spectroscopy confirmed the identity of dendrimer **1**, showing that the carbon resonances for the different segments Si–*C*H$_2$–*C*H$_2$–Si of the two generations were well defined, and that there was a slight shift for the *C*H$_3$ attached to the branching Si atom from – 5.82 in **4** to – 6.24 ppm in **1**. ^{29}Si NMR allowed further elucidation of the structure, showing a singlet at – 66.21 (T-type silicon), a singlet for the branching Si atom, appropriately shifted from – 10.99 ppm in **4** to – 1.12 ppm in **1**, and the siloxy resonances from the mesogenic segments at ~8.2–7.3 ppm, with roughly the expected ratio per arm of the silsesquioxane cage of 1 : 1 : 4, respectively.

In agreement with the ^{1}H and ^{13}C NMR spectroscopy, GPC showed a peak of low polydispersity ($M_w/M_n = 1.06$), with a shoulder at shorter elution time and a smaller peak at longer elution time, in agreement with the presence of smaller sized species. However, the M_w value was grossly underestimated, by a factor of 1.3–1.5 ($M_w = 6065$; expected for G$_1$-(cyanobiphenyl)-16-octasilsesquioxane = 9127; expected for G$_1$-(cyanobiphenyl)-14-octasilsesquioxane = 8163). A similar situation to that described above was observed for the parent dendrimer **4**, and we attribute this to the non-polar, spherical structure of **1**, that does not fit the universal calibration standards used.

The melting behaviour of the pure dendrimer **1** was investigated by a variety of techniques including thermal polarized transmitted light microscopy and differential scanning calorimetry (DSC). Examination of the defect textures of the first generation dendrimer **1** shows that it exhibits enantiotropic smectic A and smectic C phases, with the absence of crystallization and the following phase sequence; g – 17.5 SmC 63.1 SmA 91.7 I (°C). DSC confirmed the transition temperatures, but broad peaks for the transition enthalpies were obtained which is consistent with the system being microphase separated. Comparison with the linear analogue, which also exhibits enantiotropic smectic A and smectic C phases with the following sequence, g – 12.8 Cr, 4.66 Cr 39.0 SmC 74.2 SmA 102.9 I, tentatively suggests that the dendritic structure has the effect of lowering the clearing point, the SmC to SmA transition temperature and the glass transition temperature with doubling the number of mesogens per molecule. This 'non-conventional' thermal behaviour is contrary to that observed for conventional liquid crystal polymers.

The smectic A and smectic C phases exhibited by dendrimer **1** were identified from the defect textures formed on cooling from the isotropic liquid. Upon cooling, the smectic A phase separated from the isotropic liquid in the form of bâtonnets that coalesced to give a focal-conic defect texture which was characterized by elliptical and hyperbolic lines of optical discontinuity. Accompanying the focal-conic defects was the formation of a homeotropic texture. The exhibition of both of these textures is diagnostic for the presence of the smectic A phase [7]. Cooling of the smectic A phase resulted in a second order phase transition to the smectic C phase. The smectic C phase exhibited paramorphotic textures based on those of the smectic A phase. Thus the homeotropic texture became birefringent and exhibited a *schlieren* pattern with only $s = \pm 1$ singularities, whereas the focal-conic texture became broken and patched which is consistent with the mesogenic groups tilting within their layers.

Interestingly the defect texture of the smectic A phase formed easily on cooling from the isotropic liquid, indicating that the mesophase has a relatively low viscosity in comparison with linear polymeric systems, which often require annealing for several days. This is a typical result for liquid crystalline dendrimers demonstrating that they have some properties that are akin to low molar mass materials.

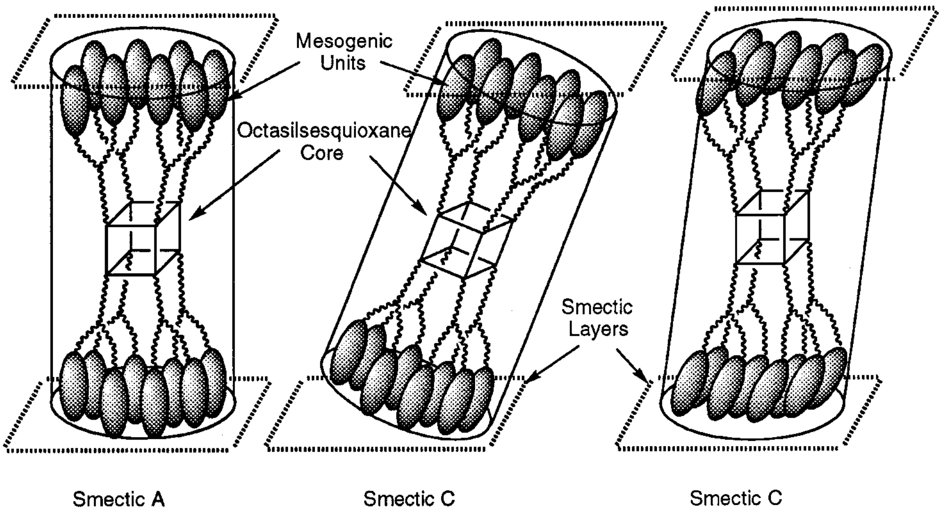


Figure 2. Possible molecular topologies enforced by the liquid crystalline environment.

The results of the mesophase characterization imply that the dendrimer must have a rod-like shape in order that it can pack in layers. Moreover the molecules within the layers must be disordered and the layer structure diffuse. Computer simulations indicate that all of the mesogenic groups cannot lie on one side of the octasilsesquioxane core, and therefore that the mesogenic arms are split into two groups with the core unit sandwiched in between, as shown in figure 2. Thus the mesophase has a quasi-bilayer structure with respect to the mesogenic unit, and a monolayer structure with respect to the octasilsesquioxane cores, and is therefore a microphase separated system. Upon cooling, either the whole molecules tilt over to form a smectic C phase or else the mesogenic units themselves tilt, which is the more likely scenario, see figure 2.

Thus, as with previous studies, we have shown that the environment of a self-organized condensed mesophase can affect molecular topology and shape. The dendrimer prepared remarkably exhibits a smectic C phase that opens the way to the synthesis of chiral systems which will inevitably exhibit non-linear properties such as ferroelectricity, pyroelectricity and piezoelectricity.

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References

[1] Newkome, G. R., Moorefield, C. N., and Vögtle, F., 1996, in *Dendritic Molecules* (Weinheim: Verlag Chemie).

[2] Lorenz, K., Hölter, D., Stühn, B., Mühlhaupt, R., and Frey, H., 1996, *Adv. Mater.*, **8,** 414; Seyferth, D., Son, D. Y., Rheingold, A. L., and Ostrander, R. L., 1994, *Organometallics*, **13,** 2682; Ponomarenko, S. A., Rebrov, E. A., Bobrovsky, A. Y., Boiko, N. I., Muzafarov, A. M., and Shibaev, V. P., 1996, *Liq. Cryst.*, **21,** 1.

[3] Jaffrès, P.-A., and Morris, R. E., 1998, *J. chem. Soc., Dalton Trans.*, 2767.

[4] Mehl, G. H., and Goodby, J. W., 1996, *Chem. Ber.*, **129**, 521 and references therein; Mehl, G. H., and Goodby, J. W., 1996, *Angew. Chem. int. Ed, Engl.*, **35,** 2641 and references therein.

[5] Karstedt, B. D., 1974, General Electrics, US-PS 3.814.730.

[6] Hampenius, M. A., Lammertink, R. G. H., and Vansco, G. J., 1997, *Macromolecules*, **30,** 266.

[7] Gray, G. W., and Goodby, J. W., 1984, *Smectic Liquid Crystals: Textures and Structures* (Philadelphia: Leonard Hill).