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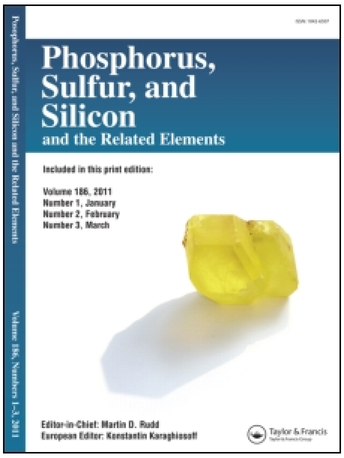

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Liquid-Crystalline Inorganic-Organic Hybrids Based on Terminally Attached Mesogens

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The results of the synthesis and the investigaiton of a number of multipodal and branched siloxane and silsesquixane liquid crystals is reported.

Keywords: Liquid Crystal; Dendrimers; Multipodes; Siloxanes; Silsequioxanes

Research into the liquid-crystalline properties of dendritic systems has made great progress over the recent years and the focus of attention has been directed mainly towards the investigation of the influence of the number generations on liquid-crystalline phase behaviour. [1,2]

Many mesomorphic dendritic systems employ the same structural elements used in liquid-crystalline side-chain polymers or multipodes, namely aromatic mesogenic groups tethered *via* hydrocarbon spacers from a scaffolding. [3] Thus the defining features for the soft phase structures are, apart from the chemical structure and the rigidity of the scaffolding, the concentration and chemical structure of the mesogenic moieties that are essential for the formation of liquid-crystalline phase behaviour and their decoupling form the scaffolding *via* spacers.

For comparative studies the number of dendrons stemming form a central core has to be varied systematically. Above a certain number small rigid cage structures approximate a centre, requiring however that the structural variation influences the liquid-crystalline phase behaviour in a defined manner. [2] In this study the siloxane and silsesquioxane scaffoldings **1** to **4** shown in Figure 1 fulfil well the criteria for a central core. The number of functional groups rises geometrically from 1 for **1** to 8 for **4**. The scaffoldings do not allow for the formation of stereoisomers or conformational isomers in the core region of the final products. The introduction of silicon containing groups into hydrocarbon liquid-crystals leads to microphase separation which has been elucidated for the scaffolds used in this study.

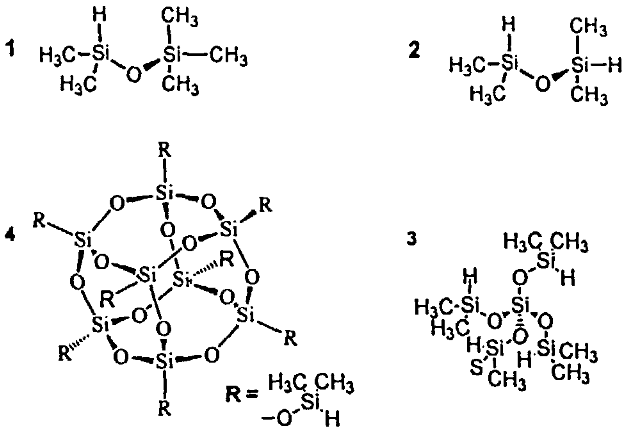

FIGURE 1 Chemical structures of the siloxane and silsesquioxane cores.

A primary target was the investigation of systems, which exhibit smectic phase behaviour. For the decoupling of mesogens, branching points and scaffolds, long spacers are required. The side-chains are depicted in Figure 2.

A malonate group was selected as a branching group because of its small size and a low tendency to complex ions, compared to other systems (*eg* amines). The cyanobiphenyl moiety was selected as a mesogenic group because of its tendency to support liquid-crystalline properties and in order to put this study in the context of related work. [3]

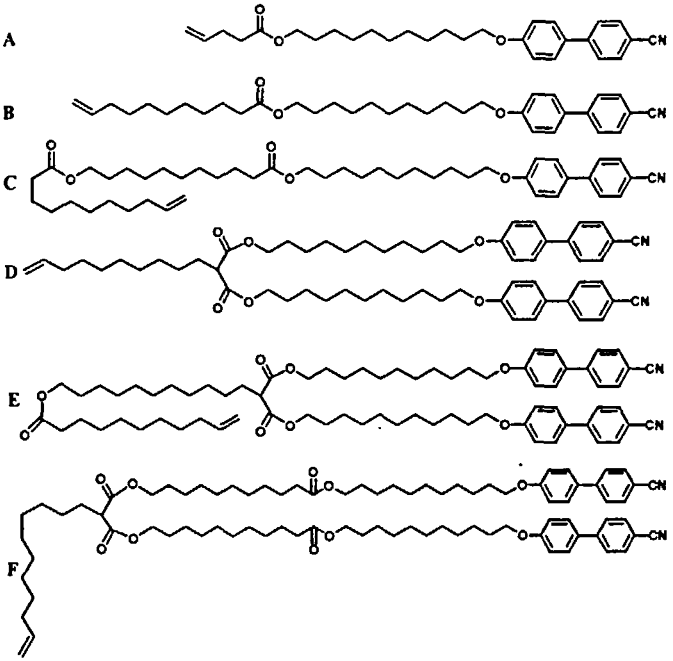

FIGURE 2: Chemical structures of the linear and branched mesogenic organic groups.

The monomers **a**, **b**, and **d** and **f** were found to exhibit smectic A phase behaviour. The hybrid systems **4a**, and the structurally related materials **1b**, **2b**, **3b**, **4b** show liquid-crystalline phase behaviour and the isotropisation temperature rises with increasing the number of liquid-crystalline side-chains attached to the predominantly inorganic cores. The isotropisation temperatures in this series ranges from 42.1 °C for **1b** to 64.2 °C **4b**. This is expected, as the materials become more polymeric in nature with ascending the series. For the materials resulting from the attachment of the side-chain **c** to the inorganic cores only crystalline phase were observed. This is attributed to the length of the alkyl chains, resulting in ratio of mesogens to hydrocarbon groups which is non-favourable for the formation of LC phases; the mesogenic content in these systems is to small for the formation of mesomorphic phase behaviour. The materials **1d**, **2d**, **3d**, **4d** show liquid-crystalline phase behaviour with clearing point ranging from 71.4 °C for **1d** to 95.7 °C for **4d**. All of the investigated materials deriving form the side-chain **e** were found to exhibit only crystalline phases. The branched materials **1f**, and **4f** exhibit layered liquid-crystalline phases (smectic A and smectic C) close to room temperature and it was observed that the clearing point for **4f** was increased to 52.5 °C compared to a much lower isotropisation temperature of 19.6 °C for the smectic A to isotropic liquid transition detected for **1f**.

Acknowledgements
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