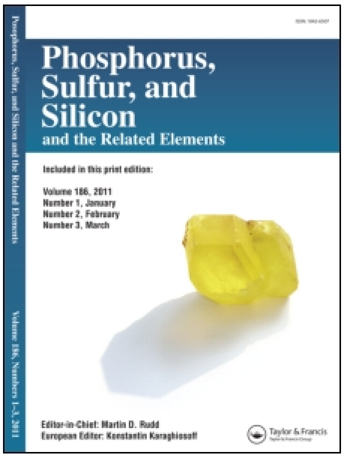

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Nematic Phase Behaviour of Inorganic-Organic Hybrid Systems Based on Dendritic Carbosilazane Cores

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The synthesis of the first inorganic-organic hybrid liquid crystal dendrimers, which exhibit enantiotropic nematic phase behaviour, is presented.

Keywords: Liquid Crystals; Dendrimers; Inorganic-Organic Hybrid Materials; Nematic Phase

Over the last five years, oligomeric and dendritic inorganic-organic materials, which exhibit thermotropic liquid crystal mesophases, have been extensively investigated. A common structural feature of most of these materials is a multifunctional inorganic core such as dendritic carbosilanes[1], silsesquioxanes[2] or fullerenes[3] from which organic mesogenic units are appended *via* appropriate spacer groups.

The mesophases found in these compounds are predominantly of the smectic type. In spite of the considerable chemical and structural variety of the materials reported to date, until very recently[4] no hybrid material was found to exhibit enantiotropic nematic phase behaviour. For side chain liquid crystal polymers[5] it has been demonstrated however that the lateral attachment of mesogens to the spacer strongly favours the formation of the nematic phase. In this paper we present the first examples of liquid crystal dendrimers with laterally attached mesogenic units, which show nematic phase behaviour.

The mesogens **1** and **2**[4] and the dendritic carbosilazanes **C**, **D** and **E**[6] were synthesised as described earlier and the carbosilazanes **A** and **B** by standard procedures (Figure 1).

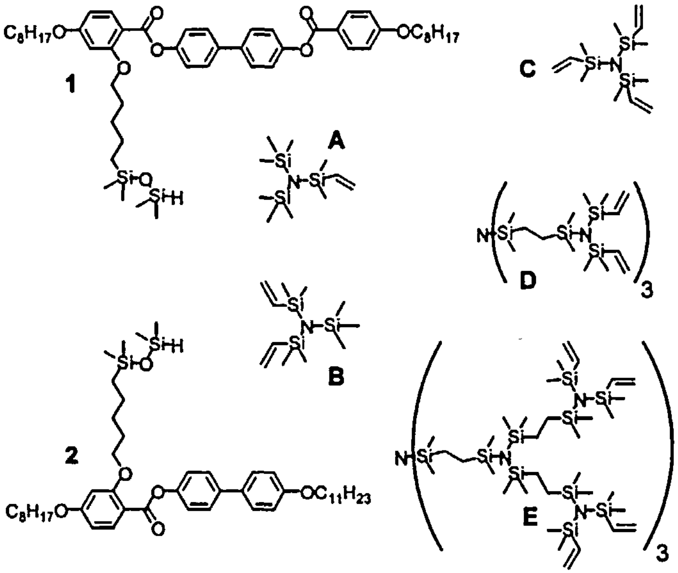

FIGURE 1 Mesogens **1** and **2** and carbosilazane core molecules **A**, **B**, **C**, **D** and **E**.

The inorganic-organic hybrids were then obtained by coupling the mesogens **1** and **2** to the core compounds **A**, **B**, **C**, **D** and **E** in a hydrosilylation reaction, thus affording **A-1**, **$B(1)_2$**, **$B(2)_2$**, **$C(1)_3$**, **$C(2)_3$**, **$D(1)_6$**, **$E(1)_{12}$**. All products were purified by column chromatography on alumina using hexane-dichloromethane mixtures as eluent and characterised by ^1H and ^{13}C NMR spectroscopy, elemental analysis, size exclusion chromatography, differential scanning calorimetry and optical polarising microscopy. The first generation dendrimer **D(1)**$_6$ is depicted in Figure 2.

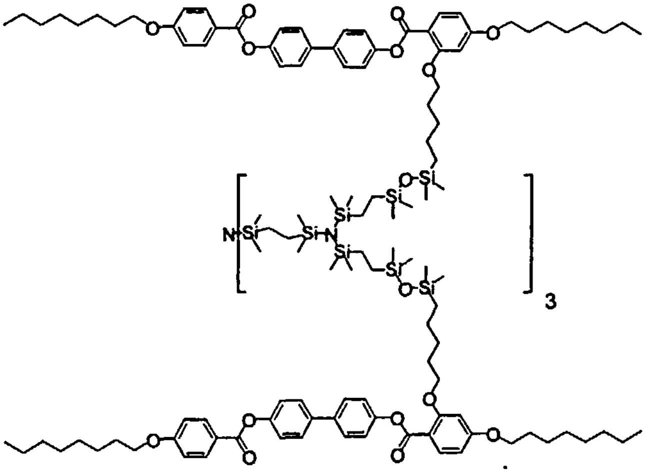

FIGURE 2 Compound **D(1)**$_6$.

The transition temperatures of the products are listed in Table 1. All these materials exhibit a nematic phase as the highest stable liquid crystalline phase characterised by a typical *schlieren* texture when observed using optical polarising microscopy.

Compound	Transition temperature (°C)
A-1	Cr 68.7 [SmC 67.1] N 98.7 Iso
$B(1)_2$	Cr 70.8 Cr 77.1 [SmC 75.3] N 121.1 Iso
$C(1)_3$	Cr 73.0 SmC 74.6 N 130.5 Iso
$D(1)_6$	Cr 58.1 SmC 74.5 N 128.8 Iso
$E(1)_{12}$	Cr 52.0 SmC 73.4 N 125.7 Iso
$B(2)_2$	Cr −12.6 N 36.5 Iso
$C(2)_3$	Tg −25.0 N 41.6 Iso

TABLE 1 Transition temperatures as determined by DSC, temperatures and phases in brackets refer to monotropic (thermodynamically non stable) phases.

All materials containing the mesogenid unit 1 exhibit smectic C phase behaviour at lower temperatures, characterised by broken focal conics and a *schlieren* texture. The phase behaviour is monotropic for the compounds **A-1** and **B(1)$_2$** and enantiotropic for the dendrimers of generation zero, one and two **C(1)$_3$**, **D(1)$_6$** and **E(1)$_{12}$**. Although the molecular weight of the molecules doubles with each subsequent generation, the mesomorphic properties and transition temperatures of the dendrimers remain remarkably similar.

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