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Dendritic and Multipodal Liquid-Crystalline Materials Based on Organic-Inorganic Hybrid Carbosilazane Cores

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The synthesis of the first inorganic-organic hybrid liquid crystal dendrimers, which exhibit enantiotropic nematic and smectic C phase behaviour is presented and the liquid-crystalline phase properties are discussed.

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

INTRODUCTION

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, 6] 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.

EXPERIMENTAL AND DISCUSSION

The mesogens **1** and **2** [4] and the dendritic carbosilazanes **C**, **D** and **E** [7] were synthesised as described earlier and the carbosilazanes **A** and **B** according to standard procedures (Figure 1).

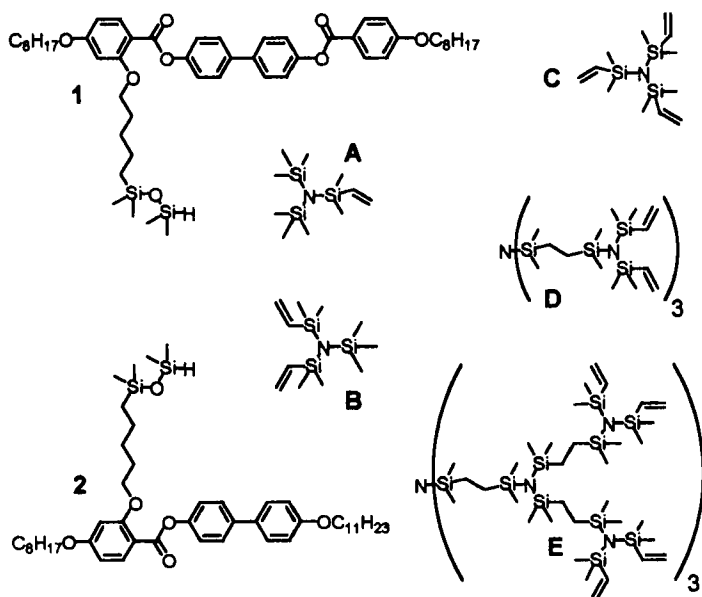
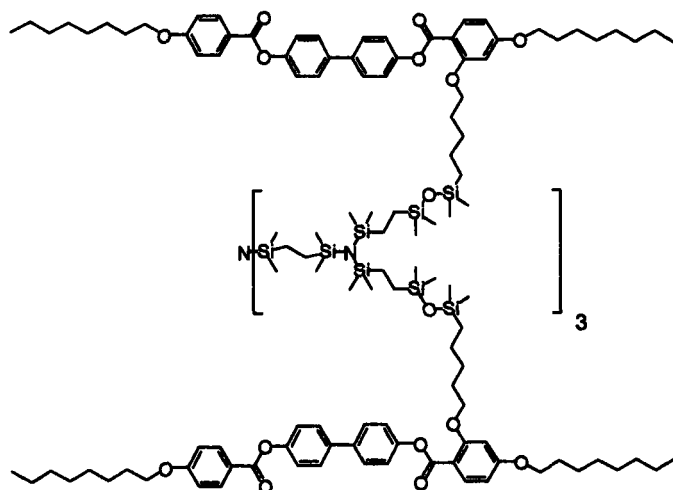


FIGURE 1 Mesogens **1** and **2** and carbosilazane core molecules **A**, **B**, **C**, **D** and **E**.

FIGURE 2 Compound $D(1)_6$.

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, mediated by a Pt-catalyst, thus affording **A-1**, **B(1)₂**, **B(2)₂**, **C(1)₃**, **C(2)₃**, **D(1)₆**, **E(1)₁₂**. All of the 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.

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.

All materials of the series containing mesogens which incorporate four aromatic rings 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.

For the first members of the series A-1, B(1)₂ and C(1)₃, a rise in melting points from 68.7 °C for A-1 to 73.0 °C for C(1)₃ and of the isotropisation temperatures of 98.7 °C for A-1 to 121.1 °C for B(1)₂ to 130.5 °C for C(1)₃ can be observed, as the materials become more polymeric in structure. These results are in line with observations for other multipodal liquid crystals [8].

The results for the dendritic materials D(1)₆ and E(1)₁₂ show a different trend. Although the molecular weight of the molecules doubles with each subsequent generation, the mesomorphic properties and transition temperatures of the dendrimers remain remarkably similar with the melting points ranging from 58.1 °C for D(1)₆ to 52.0 °C for E(1)₁₂. This is accompanied by a fall in the isotropisation temperature for the nematic to isotropic transition from 128.8 °C for D(1)₆ to 125.7 °C for E(1)₁₂. These results are in contrast to the observations for side-chain liquid crystal polymers where a strong stabilisation of the liquid crystal state, particularly for the nematic phase, with increasing the degree of polymerisation has been observed [9].

It can however be considered that for dendritic nematic systems the microphase separation of the silicon rich and carbon rich molecule parts does not enhance the stability range of the mesophase and, if these materials are to be compared with side-chain polymers the comparison with LC polymers diluted with non-mesogenic side-chains is likely to be more instructive. For materials of such a structure dilution results typically in a reduction in the stability of the mesomorphic phases.

For the investigated systems it is however interesting that the transition temperature of the smectic C phase, which ranges from 74.6 °C for C(1)₃ to 73.4 °C for E(1)₁₂ is much less affected by the increase in molecular size. This supports the view that microphase separation stabilises the liquid crystal phase behaviour for layered phases [10].

The reduction of the number of aromatic cores by one phenyl group in the mesogens leads to a dramatic reduction of the transition temperatures in the final products.

The comparison of **B(1)₂** and **B(2)₂** shows that the monotropic smectic C phase is lost altogether for **B(2)₂** and the clearing temperature of the nematic phase is reduced to 36.5°C, a reduction by 84.6 °C when compared to **B(1)₂**.

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 (Cr = crystalline; SmC = smectic C; N = nematic, Tg = glass transition temperature).

As the melting point for this system is reduced to -12.6 °C, (a reduction by 83.4 °C when compared **B(1)₂**) the compound exhibits nematic phase behaviour at room temperature. The increase of the number of mesogens to three for **C(2)₃** is associated with the loss of the crystal phase, only a glass transition at -25 °C could be observed and as expected the stability range of the nematic phase is increased to 41.6 °C, an increase 5.1 °C, when compared to **B(2)₂**. The clearing point form the nematic phase is however 79.6 °C lower than that the structurally related material **C(1)₃**.

The experimental results support the view that the selected approach: modulation the phase range and type for organic-inorganic hybrid

materials can be achieved by a systematic variation of mesogen core structure and by controlling the size and the branching of the target molecules.

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