

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

STRUCTURE-PROPERTIES RELATIONSHIPS IN A SERIES OF LIQUID CRYSTALS BASED ON CARBOSILAZANE CORES

R. Elsäßer^a, J. W. Goodby^a, G. H. Mehl^a, D.

Rodriguez-Martin^b, R. M. Richardson^b, D. J.

Photinos^c & M. Veith^d

^a Department of Chemistry, University of Hull, Hull,
HU6 7RX, Great Britain

^b H H Wills Physics Laboratory, University of Bristol,
Bristol, BS8 1TL, Great Britain

^c Department of Physics, University of Patras,
Patras, Greece

^d Institute of Inorganic Chemistry, Universität des
Saarlandes, Saarbrücken, Germany

Version of record first published: 15 Jul 2010

To cite this article: R. Elsäßer, J. W. Goodby, G. H. Mehl, D. Rodriguez-Martin, R. M. Richardson, D. J. Photinos & M. Veith (2003): STRUCTURE-PROPERTIES RELATIONSHIPS IN A SERIES OF LIQUID CRYSTALS BASED ON CARBOSILAZANE CORES, *Molecular Crystals and Liquid Crystals*, 402:1, 1-7

To link to this article: <http://dx.doi.org/10.1080/744816667>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

STRUCTURE-PROPERTIES RELATIONSHIPS IN A SERIES OF LIQUID CRYSTALS BASED ON CARBOSILAZANE CORES

*R. Elsässer, J. W. Goodby, and G. H. Mehl**

*Department of Chemistry, University of Hull, Hull HU6 7RX,
Great Britain*

D. Rodriguez-Martin and R. M. Richardson

*H H Wills Physics Laboratory, University of Bristol, Bristol,
BS8 1TL Great Britain*

D. J. Photinos

Department of Physics, University of Patras, Patras, Greece

M. Veith

*Institute of Inorganic Chemistry, Universität des Saarlandes,
Saarbrücken, Germany*

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

Keywords: carbosilazane; columnar; dendrimer; liquid crystal; multipode; nematic

INTRODUCTION

Oligomeric and dendritic inorganic-organic materials, which exhibit thermotropic liquid crystal mesophases, have been extensively investigated over the recent years. A common structural feature of most of these materials is a multifunctional inorganic or organic core such as dendritic carbosilanes [1], silsesquioxanes [2], fullerenes [3] or polyamidoamines [4]

we acknowledge the EU for funding of this project within the framework of the TMR network contract FMRX-CT97-0121.

*Corresponding author.

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 [5] no hybrid material was found to exhibit enantiotropic nematic phase behaviour. For side chain liquid crystal polymers [6,7] it has, however 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, smecticC and columnar phase behaviour.

EXPERIMENTAL AND DISCUSSION

The inorganic-organic hybrids were then obtained by coupling the mesogen **1** 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**, **C(1)₃**. The mesogenic compound **1** [5] and the dendritic carbosilazanes **C**, **D** and **E** [8] were synthesised as described earlier and the carbosilazanes **A** and **B** according to standard procedures (Figure 1).

D(1)₆ and **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 ¹³C NMR spectroscopy, elemental analysis, size exclusion chromatography confirming polydispersities of the final products with values of 1.03 or less. The solid state properties were investigated by differential scanning calorimetry (DSC), optical polarising microscopy and X-ray diffraction studies using an experimental set-up described in detail elsewhere. [9].

The transition temperatures of the products as determined by differential scanning calorimetry (DSC 7, Perkin Elmer) 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 a higher ordered liquid crystal phase, which was identified for the compounds affording **A-1**, **B(1)₂**, **C(1)₃**, and **D(1)₆** as a smectic C phase behaviour, characterised by broken focal conics and a *schlieren* texture. For compound **E(1)₁₂** the low temperature mesomorphic phase structure could not be clearly identified and required X-ray diffraction studies in order to identify the phase structure.

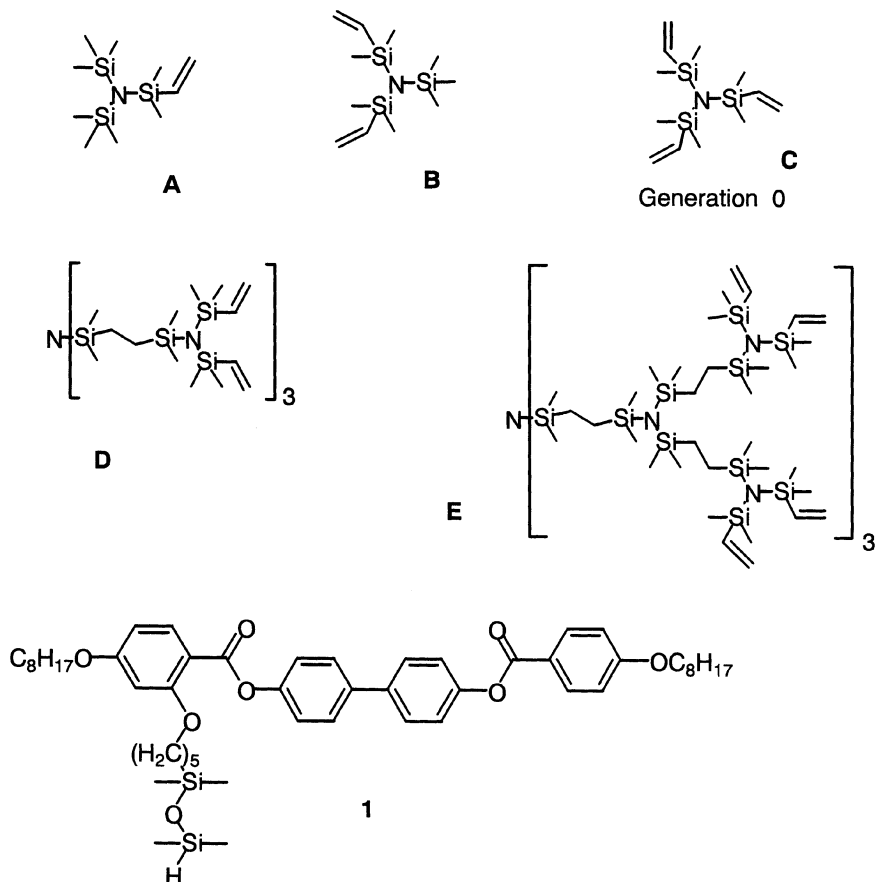


FIGURE 1 Mesogen and carbosilazane core molecules **A**, **B**, **C**, **D** and **E**.

The higher ordered liquid crystal 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.

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

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, Col = tilted columnar (hexagonal)).

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 Col 73.4 N 125.7 Iso

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 [10].

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 low temperature high ordered LC 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 [11].

The X-ray diffraction results collected from magnetically oriented samples support the phase assignment as SmC. The diffraction patterns show the typical features of diffuse wide angle intensities, associated with the intermolecular distances of the oriented mesogens and Bragg type small angle reflections at an angle to the meridian of the pattern. This angle corresponds to the tilt of the SmC phase and the position of the reflections affords the periodicity of the smectic layers. For the materials **A-1**, **C(1)₃** and **D(1)₆**, the periodicity of the smectic layers increases, from 31.5 Å for **A-1**, to 32.4 Å for **C(1)₃**, and to 33.3 Å for **D(1)₆** (Figure 2)

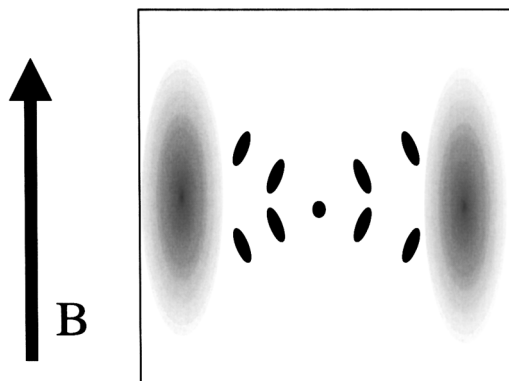


FIGURE 2 Schematic representation of the XRD pattern observed for **E(1)₁₂**; B indicates the direction of the magnetic field.

as the series of central cores is varied and ascended in size. The observed tilt angles vary between 25° to 40° , typical values for smectic C materials. The apparent tilt angle of 0° for **B(1)₂** is at present attributed to a type of anticlinic packing in a manner reported already for dimeric systems based on siloxane cores [12].

The diffraction pattern observed for **E(1)₁₂**, schematically shown in Figure 2 is different from that observed for the materials which show a smectic C phase, as the occurrence of reflections at an angle of 20° to the equator can be observed. These reflections can be indexed as the first two reflections from a hexagonal lattice (i.e. the 200/110 peak at $Q = 0.174 \text{ \AA}^{-1}$ and the 020/310 peak at $Q = 0.289 \text{ \AA}^{-1}$). The ratio of their scattering vectors, Q , is $\sqrt{3}$ within experimental error and they correspond to an intercolumnar distance of 41.6 \AA .

TABLE 2 X-ray diffraction results. The tilt angles for smectic phase are measured from the angle between the pseudo-Bragg type reflections and the meridian. For the columnar phase, the tilt angle is measured from the angle between the pseudo-Bragg type reflections and the equator of the diffraction pattern.

Compound	Temp. (°C)	Intercolumnar distance (Å)	Sm. layer spacing (Å)	Average tilt angle (degrees)
A-1	60		31.5	25
B(1) ₂	60		34.0	0
C(1) ₃	30		32.4	26
D(1) ₆	30		33.3	40
E(1) ₁₂	60	41.6		20

TABLE 3 X-ray diffraction data for compound **E(1)₁₂**

Temp (°C)	Q(200/110) /Å ⁻¹	Q (020/310) /Å ⁻¹	Inter columnar distance (Å)
70	0.179	0.303	40.5
60	0.174	0.289	41.6
40	0.170	0.293	42.7
20	0.168	0.291	43.0

The absence of reflections associated with the formation of smectic layers excludes the description of this phase as smectic F. Hence a packing structure is suggested where the central carbosilazane cores assemble in columns which are tilted with regards to the mesogens, which are not assembled in layers.

Data for the temperature dependant variation of the intercolumnar distances determined for compound **E(1)₁₂** is listed in Table 3. With decreasing the temperature from 70°C to 20°C an increase of the intercolumnar distance from 40.5 Å to 43.0 Å by 2.5 Å could be observed. This increase of the lattice could be attributed to the larger prevalence of trans conformations in the aliphatic groups at the lower temperatures and a decrease in the number of gauche conformations; alternatively a larger degree of nano-phase separation between the silicon rich part of the molecules and the hydrocarbon rich features could be responsible for this arrangement.

The unusual self-assembly behaviour of these systems is supported by the data collected for the compound **D(1)₆** in the smectic C phase. Whereas at 60°C a layer spacing of 31.4 Å could be observed, the data collected at 30°C indicates a periodicity of the layers of 33.2 Å. This increase of the layer spacing by 1.8 Å with decreasing temperature is highly unusual for materials exhibiting a smectic C phase, as the increase in tilt is expected to result in layers. However, for low molar mass systems incorporating siloxane end-groups a similar trend in the layering has been observed and the this behaviour has been associated with the microphase separating effects of the siloxane groups, crucial in modulating the self assembly behaviour of such systems. [11,12]

The experimental results for this series of materials support the view that the selected approach of lateral attaching mesogenic groups to an inorganic-organic hybrid is an effective means of modifying the liquid crystal phase range and structure. For the lower members of this systematic series nematic and smectic C phase behaviour was observed, the material based on a second generation carbosilazane core allowed the detection of nematic and columnar phase behaviour.

REFERENCES

- [1] Ponomarenko, S. A., Rebrov, E. A., Bobrovsky, A. Yu., Boiko, N. I., Muzafarov, A. M., & Shibaev V. P. (1996). *Liq. Cryst.*, **21**, 1; Lorenz, K., Hölter, D., Stühn, B., & Mülhaupt, R. (1996). *Adv. Mater.*, **8**, 414.
- [2] Mehl, G. H. & Saez, I. M. (1999). *Appl. Organomet. Chem.*, **13**, 261.
- [3] Chuard, T., Deschenaux, R., Hirsch, A., Schönberger, H. (1999). *Chem. Commun.*, 2103.
- [4] Marcos, M., Gimenez, R., Serrano, J. L., Donnio, B., Heinrich, B., & Guillon, D. (2001). *Chem. Eur. J.* **7**, 1006; Barbera, J., Marcos, M., & Serrano, J. L. (1999). *Chem. Eur. J.*, **5**, 1834.
- [5] Elsässer, R., Mehl, G. H., Goodby, J. W., & Photinos, D. J. (2000). *Chem. Commun.*, 851; Elsässer, R., Mehl, G. H., Goodby, J. W., & Veith, M. (2001). *Angew. Chem. Int. Ed.*, **40**, 2688.
- [6] Hessel, F. & Finkelmann, H. (1985). *Polym. Bull.*, **14**, 3751.
- [7] Gray, G. W., Hill, J. S., & Lacey, D. (1991). *Mol. Cryst. Liq. Cryst.*, **197**, 43.
- [8] Veith, M., Elsässer, R., & Krüger, R.-P. (1999). *Organometallics*, **18**, 656.
- [9] Richardson, R. M., Ponomarenko, S. A., Boiko, N. I., & Shibaev, V. P. (1999). *Liq. Cryst.*, **26**, 101.
- [10] Stevens, H., Rehage, G., & Finkelmann, H. (1984). *Macromolecules*, **17**, 851.
- [11] Ibn-Elhaj, M., Coles, H. J., Gouillon, D., & Skoulios, A. (1993). *J. Phys. (Paris) II*, **3**, 1807.
- [12] Carboni, C. & Coles, H. (1999). *Mol. Cryst. Liq. Cryst.*, **328**, 349.