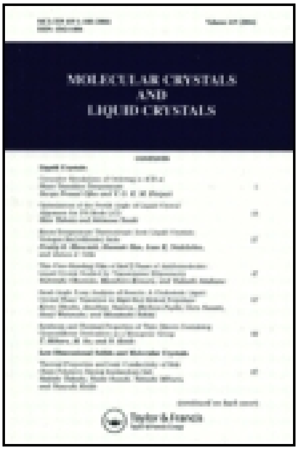

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X-Ray Diffraction from Liquid Crystalline Carbosilane Dendrimers

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We have studied the structure of two series of liquid crystalline dendrimers based on the carbosilane dendritic matrix. Generations 1 to 5 have been investigated for the series with cyanobiphenyl mesogenic groups and generations 1 to 4 for the series with methoxyphenyl benzoate mesogenic groups. Generations 1 to 4 of both series show a diffraction pattern corresponding to a simple smectic phase with disordered layers indicating that the tendency of the mesogenic units to form smectic layers overcomes the restrictions imposed by the globular dendritic core of the molecule. The variation of layer spacing with temperature and generation number indicates that there are subtle differences in the packing of the mesogens in the different samples. The 5th generation of the dendrimers with cyanobiphenyl groups shows the same smectic structure below 40°C but at higher temperatures there is some in-plane structure that suggests that columns may be formed. This can be rationalised in terms of the molecular shape becoming more spherical at higher temperatures. Above 121°C there is only a broad peak implying that this mesophase has short-range order (or possibly D_{hd} phase) until it becomes isotropic at 135°C.

Keywords: liquid crystal dendrimers; smectic mesophase; columnar mesophase; X-ray diffraction

INTRODUCTION

In this paper we report X-ray diffraction studies of two series of liquid crystalline dendrimers that have been synthesised recently[1-4]. The molecules consist of a branched carbosilane core with each chain terminated with a calamitic mesogenic unit. There is a competition between the cores, which have a roughly spherical shape, and the mesogenic units which tend to form liquid crystal phases. Attaching the mesogenic units to the dendritic core with flexible spaces reduces this conflict. The aims of this work are to confirm the phase assignments that have been made using optical microscopy and to investigate the structure of these materials at a molecular level.

EXPERIMENTAL

X-ray Apparatus

The X-ray diffraction experiments were performed on a purpose built diffractometer at Bristol. Nickel filtered copper Kα radiation from a 1.5kW sealed tube source was detected by a multi-wire two-dimensional position sensitive detector[5]. This has a resolution of 0.5x0.5 mm. And was placed at about 800mm from the sample for accurate d measurement of smectic layer spacing and at about 180mm to capture the wide-angle diffraction as well. The detector response was measured using fluorescence from a cobalt foil sample in the beam or radiation from an iron-55 source placed in the sample position. For the 800mm distance the air scattering and absorption was reduced by using evacuated paths for the incident and scattered beams. The detector was interfaced to a VAX computer for data storage and analysis.

Sample Preparation

The samples were prepared for the diffraction measurements by melting them into a 1mm thick disk shaped cavity and sealing between two 25 μm thick polyimide windows. They were aligned by cooling from the isotropic phase in a 9.4T magnetic field.

Samples

A typical molecular structure for the materials studied is the following:

$$Si\{CH_2CH_2CH_2Si(CH_3)[CH_2CH_2CH_2Si(CH_3)[CH_2CH_2CH_2X]_2]_2\}_4$$

where X represents a mesogenic unit with spacer. This material is a second generation dendrimer because, in addition to the four-functional core, there are two extra steps which each introduce a two-fold branching so that there is a total of 16 mesogenic units. Different generations may be represented by changing the number of brackets that are "nested". For simplicity we will represent dendrimers with different numbers of generations using the notation: G-*n*(X)*m* where *n* is the generation number (2 in the above example) and *m* is the number of terminal mesogenic groups (16 in the above example). In this work we have investigated two series of dendrimers:

(i) The first four generations with a methoxy phenyl benzoate ester as mesogenic unit:
$X=Si(CH_3)_2OSi(CH_3)_2(CH_2)_{11}COOPhCOOPhOCH_3$ or und-MPhB.
I.e. G-1(und-MPhB)$_8$ to G-4(und-MPhB)$_{64}$ whose synthesis and phase behaviour are described in references 1 and 4.

(ii) The first five generations with a cyanobiphenyl as mesogenic unit:
$X=Si(CH_3)_2OSi(CH_3)_2(CH_2)_{11}COOPhPhCN$ or und-CB.
I.e. G-1(und-CB)$_8$ to G-5(und-CB)$_{64}$ whose synthesis and phase behaviour are described in references 2 and 3.

In addition we have also investigated a cyanobiphenyl dendrimer with a shorter pentyl spacer rather than the undecyl spacers used in the series above I.e. G-4(pent-CB)$_{64}$.

RESULTS AND DISCUSSION

Phase identification

All of the dendrimers gave diffraction patterns that indicated an aligned smectic phase with disordered layers. Figure 1 is a typical example of a wide-angle diffraction pattern that shows the diffuse outer peaks from correlation between molecules within the same layer and sharp layer reflections at small angles. The diffraction patterns were inspected carefully for evidence of a tilted (e.g. Sm C) phase but none was found. The layer reflections had an azimuthal spread of ~15° but were at 90° to the diffuse peaks. There was not evidence of the "4-spots" pattern that would be shown by smectic C phases when the molecules remain parallel to the aligning field but the layers tilt. Azimuthal plots of the intensity in the diffuse peaks only showed two maximum rather than the four that would be displayed by a smectic C when the layer orientation remains constant during cooling from smectic A but the molecules tilt.

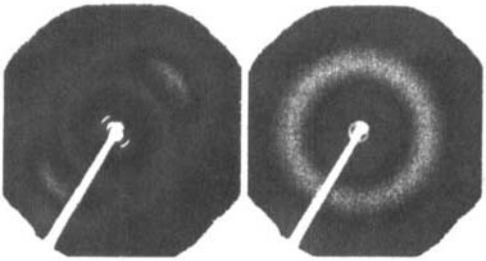

Figure 1 Diffraction patterns from G-2(und-MPhB)$_{16}$; Smectic at 36°C (left) and Isotropic, at 86°C (right).(See Color Plate II at the back of this issue)

The variation of layer spacing with temperature is another possible source of evidence for a smectic C phase. Figure 2 shows the layer spacing of G-2(und-MPhB)$_{16}$ which is believed to have a Sm C to Sm A transition at 60°C. There is clearly not sudden change in the slope of the plots at 60°C which means that any Sm C phase must have a similar tilt to the Sm A but be distinguished from it by azimuthal ordering of the molecules rather than the onset of a tilt of their long axes with respect to the layer normals. The X-ray diffraction reported here does not confirm the presence of a Sm C. However there is good evidence from microscopy and calorimetry (see e.g. reference 4) for a Sm C phase in the G-*n*(und-MPhB) series so we conclude that any tilted phase in these materials must have a low tilt angle change at the transition. An angle change of less than ~10° would be impossible to observe without better sample alignment.

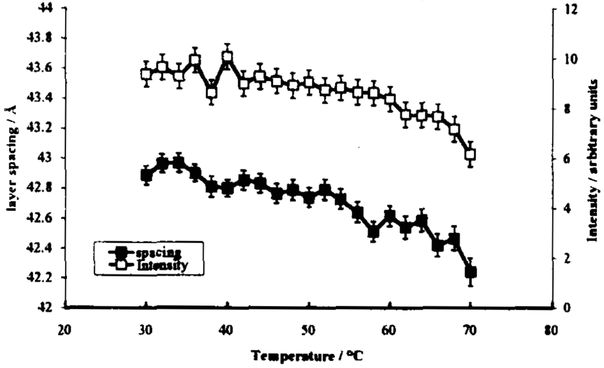

Figure 2 Smectic layer-spacing and Bragg peak intensity as a function of temperature for G-2(und-MPhB)$_{16}$ during cooling.

Most of the dendrimers studied showed diffraction patterns consistent with a smectic phase with disordered layers from room temperature to the isotropic phase. The G-5(und-CB) was exceptional in that is showed other structures above room temperature and it is discussed further below. The structures formed below room temperature were not investigated. Many of the dendrimers showed a change in the intensity of the layer reflections at 50-60°C when aligned samples were used. This was not observed in unaligned "powder" samples and results from a change in the orientation of the sample at this temperature. This might be due to a softening of the material at this temperature.

Effect of Generation number

The smectic layer spacings for all the materials studied are plotted in figure 3. For most samples the spacing varied by about 0.5Å across the temperature range so the values at 40°C have been used.

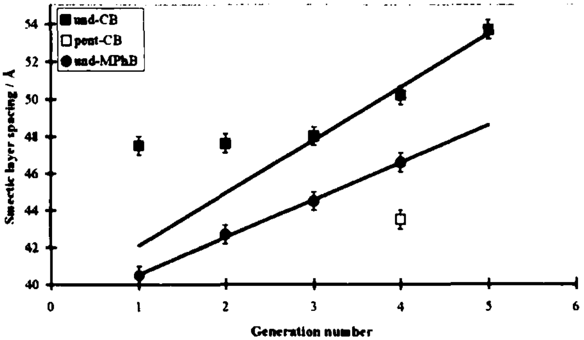

Figure 3 The smectic layer spacings for the different generations of dendrimers

There are several inferences that can be made from the results in figure 3.

(i) The layer spacings are in reasonable agreement with those expected for a smectic phase. However since the MPhB moiety is longer than the CB one it must be more fully interdigitated as shown in figure 4. Partial overlapping of cyanobiphenyl groups results from the interaction between the strong CN dipole and the polarizable benzene rings and is well known in liquid crystals[6].

(ii) For the MhB series there is an increment of 2Å for each generation number which is considerably less than the stretched length of two $Si(CH_3)CH_2CH_2CH_2$ units(~10 Å). This suggests that the flexible spacers compensate for the orientation of the dendrimer links at the outer part of the core. If the spacers were completely flexible, the contribution of the dendrimer core to the layer thickness would be approximately the volume of the dendrimer core divided by the area occupied by the mesogenic units. This can be estimated as follows. The volume of the dendrimer core, V_d, is given by the equation:

$$V_d \approx V_l \; (4 + 4\sum_{g=1}^{n} 2^g).$$

where V_l is the volume of one $Si(CH_3)(CH_2CH_2CH_2)$ unit and is estimated to be 145Å^3 from the typical carbosilane density of ~1g cm^{-3}. The area, $A_{mesogen}$, occupied by a mesogenic unit is given by the equation:

$$A_{mesogen} = d^2 \frac{2}{\sqrt{3}}$$

where d is the inter-mesogen distance of about 4.5Å. If space is filled by the dendrimer core and flexible spacer the contribution to the layer thickness from the dendrimer, $d_{dendrimer}$, will be given by the equation:

$$d_{dendrimer} = \frac{V_l(4+4\sum_{g=1}^{n}2^g)}{2^{n+2}A_{mesogen}}$$

This equation predicts that $d_{dendrimer}$ changes by only 3Å on going from n=1 to 4 which is less than the observed d-spacing change of 6Å. However a ~30Å change would be expected if the dendrimers and spacers were fully stretched in the radial direction. This suggests that the flexibility of the spacers do partially compensate for the orientation of the chain at the outside of the dendrimer units in order to fill space and improve packing of the mesogenic units.

(iii) Comparison of the layer spacing for the G-4(pent-CB)$_{64}$ and G-4(und-CB)$_{64}$ supports the interpretation that the flexible chains are disordered to accommodate the conflicting tendencies of the dendritic core and the mesogenic units. The difference in layer spacing is only 7 Å which is much less than the length of two stretched $(CH_2)_6$ units (~15Å)

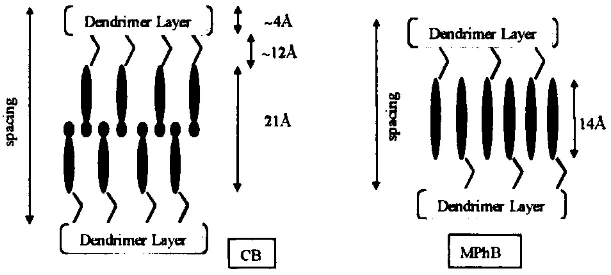

Figure 4 Schematic diagram of packing in the two series of dendrimers with approximate dimensions from molecular models.

(iv) For low generation numbers the layer spacing in the und-CB series is almost independent of the generation number. This may be due to a compensating change in the degree of interdigitation with the CN interacting with the first benzene ring in the first generation dendrimer but tending to interact with the second at higher generation numbers. This may be a result of the small size and high surface curvature of the first generation dendritic core that would not favour overlap of the mesogenic units. Higher generations would have less curvature and hence permit a larger proportion of the mesogenic units to overlap more.

Results from G-5(und-CB)$_{128}$

The small angle X-ray scattering (SAXS) from G-5(und-CB)$_{128}$ has been discussed in detail in reference 3 and so only the main results are discussed here. Below 40°C the scattering is the same as that from the previous generations (G-1(und-CB)$_8$ to G-4(und-CB)$_{64}$) and corresponds to a smectic phase with disordered layers. In the temperature range 40 to 121°C new peaks appear in the scattering pattern and they can indexed as a hexagonal unit cell whose dimensions (a , the in-plane inter-dendrimer distance and c, the layer spacing) vary with temperature as shown in figure 5. This is analogous to the crystal B phase but with elongated dendrimer units instead of calamitic molecules. The temperature dependence suggests that the elongation along the layer normal at low temperature reduces as the temperature is increased and the dendrimers become more globular. Unfortunately this indexing scheme is not unique and it has not proved possible to eliminate the possibility that the columns are formed within the layers rather than perpendicular to them. However whichever structure turns out to be the correct one, it is clear that some in-plane inhomogeneity is developing as the temperature increases.

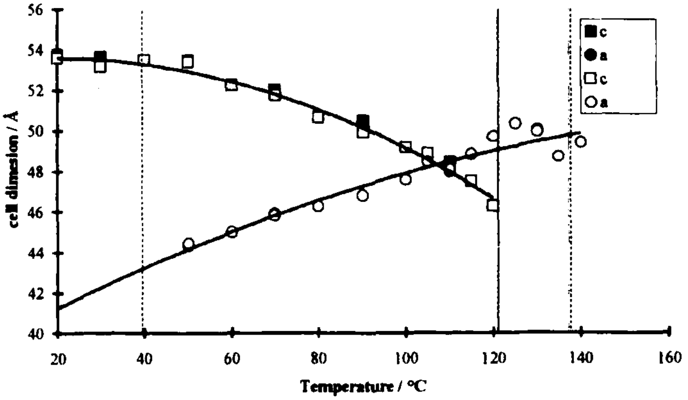

Figure 5 Showing the dimensions for the hexagonal unit cell formed by G-5(und-CB). The open and closed markers result from two different series of measurements.

In the upper mesophase, (121 to 135°C) only one slightly broadened peak remains. The Q value of this broadened peak extrapolates from the 100 peak of the phase below 121°C. It is therefore reasonable to suppose that the upper mesophase has a columnar structure with disordered columns and a hexagonal net of columns (D$_{hd}$). The columns can move freely parallel to one another and the lamellar characteristics have entirely disappeared.

CONCLUSION

It has been shown that both series of liquid crystal dendrimers form normal smectic phases despite the globular geometry of the dendritic core. Although the mesogenic units form a layer, the flexible spacers are not perfectly oriented parallel to the layer normal. They are probably distorted by the requirement to fill space and to link the layer of mesogens to a globular core. Both the methoxyphenyl benzoate and the cyanobiphenyl mesogenic units are interdigitated although the cyanobiphenyl units do not completely overlap. The G-5(und-CB) dendrimer shows in-plane structure of the layers which probably develops into a columnar structure at high temperatures.

References

[1] S.A. Ponomarenko, E.A. Rebrov, A.Yu. Bobrovsky, N.I. Boiko, A., M. Muzafarav and V. P. Shibaev. *Liquid Crystals*, **21**, 1–11 (1996)

[2] S.A. Ponomarenko, E.A. Rebrov, N.I. Boiko, A.M. Muzafarav and V.P. Shibaev. *Polym. Sci.* A 40,763–774 (1998)

[3] R.M. Richardson, S.A. Ponomarenko, R.M. N.I. Boiko, V.P. Shibaev, submitted to Liquid Crystals 1998

[4] S.A. Ponomarenko, N.I. Boiko, E.A. Rebrov, A.M. Muzafarov, I.J. Whitehouse, R.M. Richardson and V.P. Shibaev, this conference.

[5] J.E. Bateman, J.F. Connolly, R. Stephenson, A.C. Flesher, C.J. Bryant, A.D. Lincoln, P.A. Tucker and S.W. Swanton, Nuc. Inst. And Methods in Physics. Res. A259, 506 (1987)

[6] A.J. Leadbetter, R.M. Richardson and C.N. Colling, *J. Physique* **36,** C1–37 to 43 (1975)