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Liquid crystalline dendrimer of the fifth generation: From lamellar to columnar structure in thermotropic mesophases

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The structure of a liquid crystalline (LC) carbosilane dendrimer of the fifth generation bearing 128 terminal cyanobiphenyl mesogenic groups has been studied. This dendrimer was synthesized by a hydrosilylation reaction and then the cyanobiphenyl mesogenic groups were chemically linked to the dendritic matrix via a $-OOC-(CH_2)_{10}-Si(CH_3)_2OSi(CH_3)_2-$ spacer. Structural studies carried out by polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction methods revealed unusual phase behaviour. At room temperature the dendrimer forms a lamellar (smectic A) phase which develops in-plane ordering above 40°C. This is due to a tendency to form columns of molecules which are probably perpendicular to the layers. Above 121°C the material transforms into another more disordered mesophase which is probably a disordered hexagonal columnar phase. The proposed structures and molecular packing in these different types of mesophase are discussed.

1. Introduction

Currently, there is growing interest in the synthesis and investigation of systems with unusual molecular structure showing mesomorphic properties, such as liquid crystalline (LC) dendrimers [1–8], TGB* chiral phases [9] and different sanidic systems [10]. Recently LC dendrimers with highly branched structures and a regular architecture have been attracting much attention. Their molecules combine structural units capable of liquid crystal mesophase formation (mesogenic groups) [11] with a dendritic (superbranched) or 'cascade' architecture [12, 13].

Two different types of LC dendrimer can be distinguished, depending on the location of structural units in the molecule. They are LC dendrimers with mesogen-containing branching units and LC dendrimers with terminal mesogenic groups. The former contain mesogenic units distributed throughout the whole volume of the dendritic molecules. Recently it was shown that such LC dendrimers form calamitic nematic and smectic thermotropic LC mesophases [1]. The latter have mesogenic groups only on the 'surface' of the dendritic molecules. Until now, only lower generations‡ of this type have been investigated [2–5]. These compounds form thermotropic mesophases of the smectic type (SmA or SmC) only. In addition it has been shown that some monodendrons without mesogenic groups can self-assemble into cylindrical [6] and spherical [7] supramolecular dendrimers which produce columnar and cubic mesophases, respectively.

This paper describes the first example of an LC dendrimer with terminal mesogenic groups forming a columnar thermotropic mesophase. Using differential scanning calorimetry (DSC), X-ray diffraction data and polarizing optical microscopy we have revealed an unusual phase behaviour of the dendrimer. The transition from a lamellar to a columnar structure proceeds in the same LC dendrimer simply due to the temperature changing (thermotropic polymorphism).

2. Results and discussion

This work deals with the fifth generation (G-5) of carbosilane dendrimer bearing 128 terminal cyanobiphenyl (CB) groups $G\text{-}5(\text{Und-CB})_{128}$§ (figure 1). Synthesis of the dendrimer has been described in detail elsewhere [8]. A carbosilane dendrimer with the same number of allyl terminal groups was used as the dendritic matrix. Cyanobiphenyl mesogenic groups were linked to it through $-OCC-(CH_2)_{10}-Si(CH_3)_2OSi(CH_3)_2-$ spacers

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[‡] Generation number can be defined as the number of branching layers in a spherically symmetrical molecule of dendrimer.

[§] In the formula $G-n(X)_m$, n is the generation number and m is the number of terminal groups X shown in the parenthesis.

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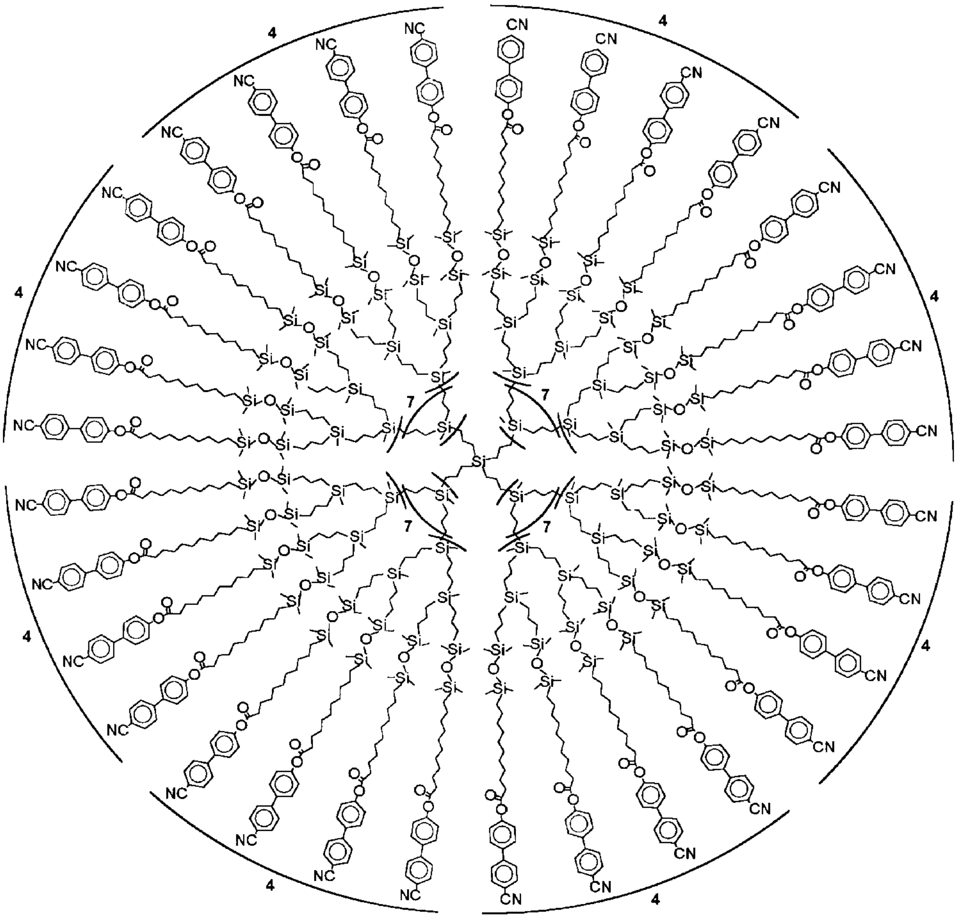


Figure 1. Structural formula of fifth generation of carbosilane dendrimer with 128 terminal cyanobiphenyl groups G-5(Und-CB)$_{128}$.

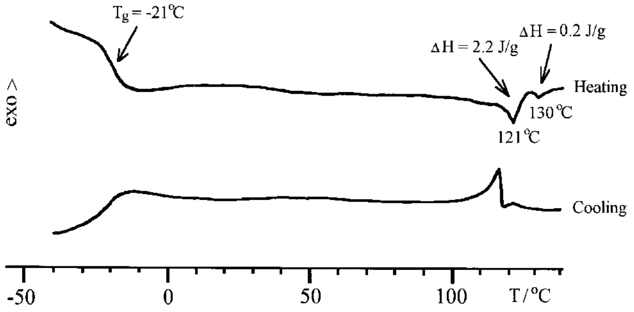


Figure 2. Second heating and first cooling DSC traces of LC dendrimer G-5(Und-CB)$_{128}$.

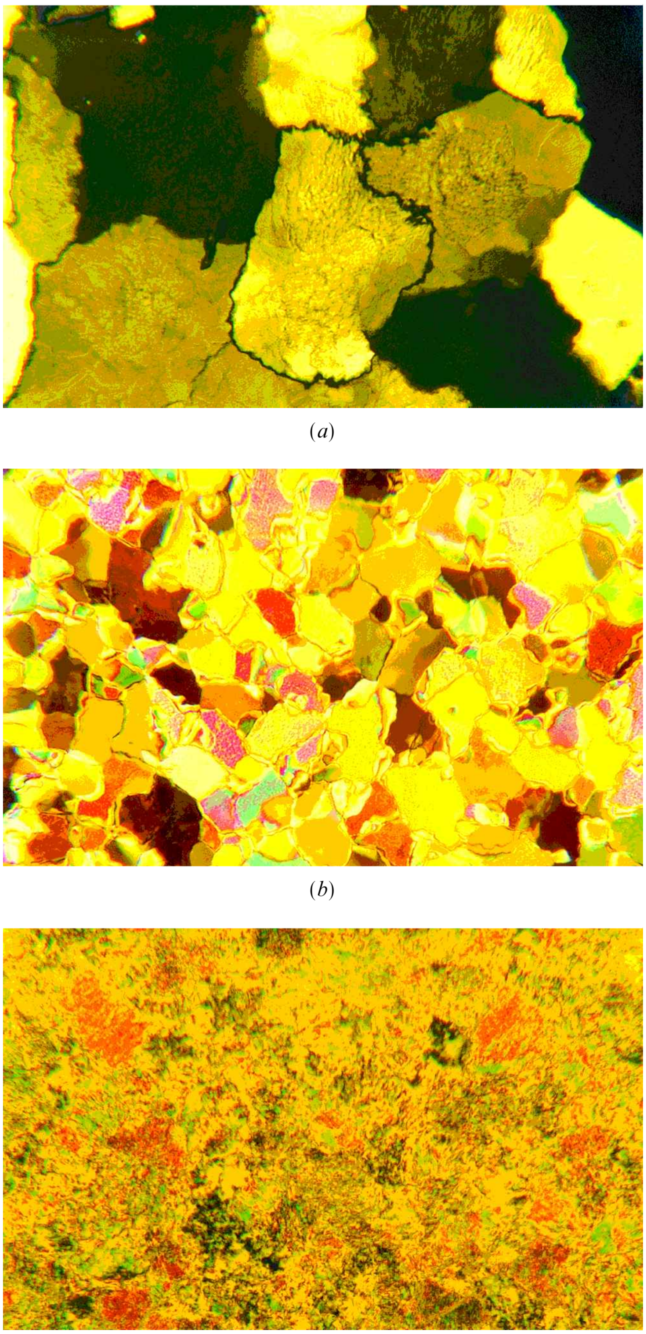
(using undecanoyl residue, Und) by a hydrosilylation reaction. The structure of the new compound was proved by ^{1}H NMR spectroscopy and GPC methods. The polydispersity of the dendrimer was less then 1.03.

2.1. *Thermal behaviour*

The thermal behaviour and structure of this LC dendrimer were investigated by means of polarizing optical microscopy and DSC in combination with small and wide angle X-ray scattering (SAXS and WAXS).

Aside from the glass transition at −21°C, the DSC heating curve shows two first order phase transitions: one peak at 121°C with an enthalpy of 2.2 J g^{-1} and another peak at 130°C with an enthalpy of 0.2 J g^{-1} (figure 2). It is worthy of note, that the enthalpy of the first peak, corresponding to the transition from one type of mesophase to the other one, is about ten times more then the enthalpy of the second peak, corresponding to the transition from the high temperature mesophase to the isotropic melt. Moreover, the latter enthalpy value is extremely low (0.2 J g^{-1}). From the DSC cooling curve it is seen that all transitions are reproduced with some supercooling. In order to find the difference between the phases observed, let us consider the results of the polarizing optical microscopy investigations.

Polarizing optical microscopy shows three different textures depending on the temperature (figure 3). In the range 120–135°C a dull grey-yellow mosaic texture is seen, figure 3 (*a*). However a bright coloured mosaic texture is observed in the range 70–119°C, figure 3 (*b*). On cooling the sample below 70°C this mosaic texture


(a)

(b)

(c)

Figure 3. Optical polarizing photomicrographs of characteristic textures of LC dendrimer G-5(Und-CB)$_{128}$ at different temperatures (magnification ×200): (*a*) grey-yellow mosaic texture at $T = 124$°C; (*b*) coloured mosaic texture at $T = 113$°C; (*c*) 'broken' mosaic texture at $T = 20$°C.

is gradually destroyed, figure 3 (*c*). It should be noted that the transition from one phase to another one at 119°C proceeds through the complete disruption of the former. On heating the mosaic texture until 119°C it becomes almost isotropic. Further heating or annealing leads to the formation of a new anisotropic phase with weak birefringence—the larger scaled grey-yellow mosaic texture, figure 3 (*a*)—which transforms into the isotropic melt at 135°C. On cooling, this former phase transition occurs as follows. On the weakly birefringent mosaic of the high temperature anisotropic phase, bright germs of spherulites of the lower temperature phase appear and grow very fast, forming the bright coloured mosaic texture, figure 3 (*b*). These results mean that upper and lower phases corresponding to figures 3 (*a*) and 3 (*b*), respectively, must have completely different structures.

It is well known from the literature, that a mosaic texture is characteristic of ordered smectic, some cubic¶ and columnar mesophases [14]. If the phase is smectic, it shows that not only are smectic layers present in the phase, but also that some elements of ordering exist within the layers. In other words, it means that a mosaic texture is characteristic of probably a more ordered structure than that of smectic A or smectic C mesophases. In order to understand the structural types of the mesophases formed by this LC dendrimer let us consider the SAXS results.

2.2. *Structure of G-5 (Und-CB)$_{128}$ mesophases*

The small angle X-ray scattering (SAXS) from an unaligned sample of G-5(Und-CB)$_{128}$ at different temperatures is presented in figure 4. As can be seen, up to four different Bragg peaks can be observed. At 30°C only peaks 1 and 4 occur at $Q = 0.115$ Å^{-1} and $Q = 0.230$ Å^{-1} and their Q-values increase with temperature. They correspond to the first and second order reflections from a lamellar structure (smectic A mesophase with a layer spacing of 54 Å at 30°C). Their intensities decrease with increasing temperature and they disappear completely at 121°C.

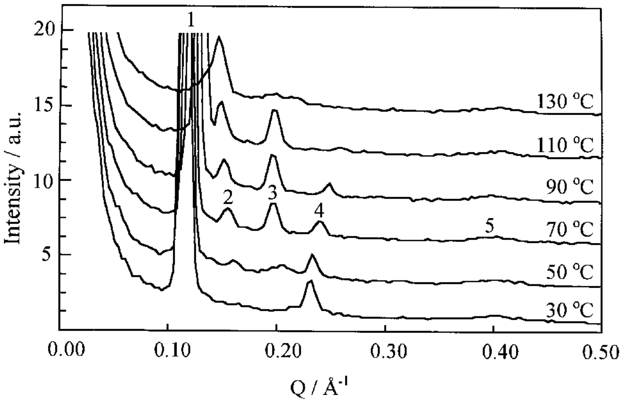


Figure 4. Small angle X-ray scattering from G-5 (Und-CB)$_{128}$ at different temperatures.

¶For instance, blue phases.

Peaks 2 and 3 appear only above 40°C and they exist until the transition at 121°C. Peak 2 persists above the transition although it becomes slightly broader and weaker. No change in this peak was observed at the temperature corresponding to the transition to the isotropic phase. The intensities of peaks 2 and 3 are much weaker than the intensity of peak 1 and they have different temperature dependencies. The position of peak 2 is shifted to lower Q with increasing temperature, while peak 3 is temperature independent. The ratio (Q_3/Q_2) is close to 1.22 ($\approx \sqrt{1.5}$) which would suggest a cubic or hexagonal phase. However the ratio is slightly temperature dependent and is actually significantly larger then 1.22, so this possibility must be rejected. Incidentally peaks 1 and 4 tend to align partially parallel to a 9 T magnetic field applied to the sample during slow cooling from the isotropic phase. The other peaks tend to align at intermediate angles. Peak 5 (at $Q = 0.4\,\text{Å}^{-1}$) is present in all the phases, but is not a Bragg peak, being rather broad and weak. Another broad peak is observed in the mesophases at wide angles ($Q = 1.15$ to $1.20\,\text{Å}^{-1}$) which corresponds to a lateral spacing of about 5 Å, typical of phases such as smectic A formed by calamitic molecules.

These results for the temperature range 40 to 121°C can be explained as following. Peaks 1 to 4 can be indexed as a two-dimensional rectangular unit cell whose dimensions (a, in-plane and c, the layer spacing) vary with temperature as shown in figure 5. The observed and calculated reciprocal lattice vectors at 70°C are presented in the table; they correspond to a rectangular cell with the dimensions of 39.7 × 52.0 Å. It should be noted that only low order peaks are observed which indicate a very disordered structure. No Bragg peaks involving a third crystallographic axis (b) were observed. There are two possible explanations of this.

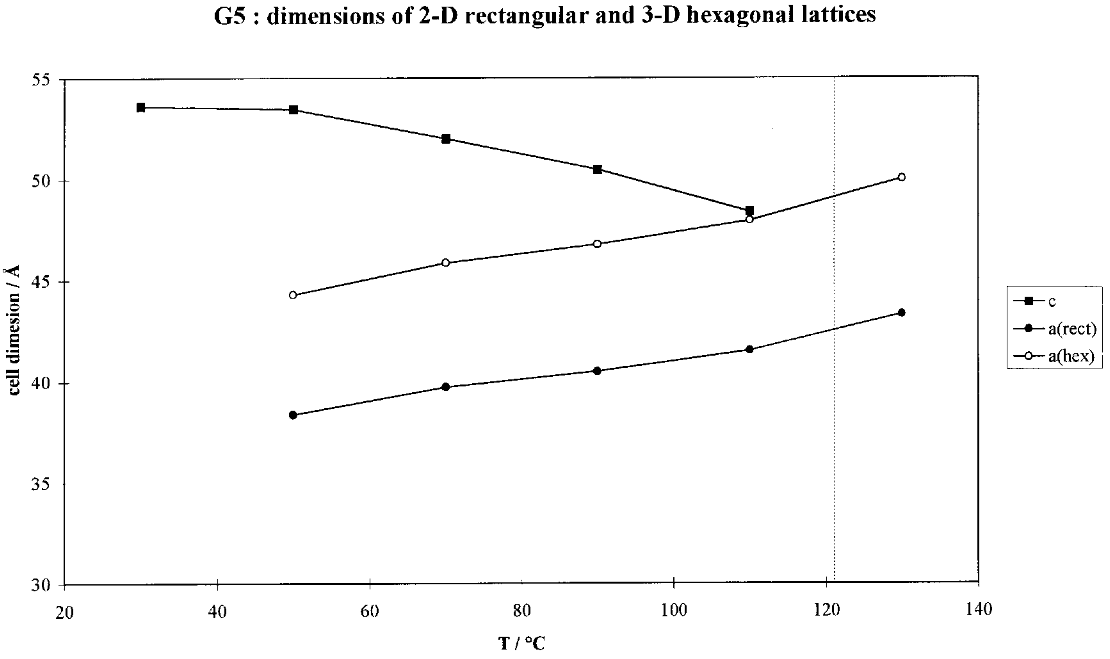


Figure 5. Temperature dependence of lattice parameters derived from the positions of the Bragg peaks 1 to 4 assuming either a two-dimensional rectangular lattice or a three-dimensional hexagonal lattice. The parameter corresponding to the position of peak 2 in the upper mesophase is also shown.

Table. Q values measured from the material at 70°C and calculated for a rectangular unit cell with a(rect) = 39.7 Å and c = 52.0 Å. Note that peak 5 is only a diffuse maximum, but it appears at twice the Q of peak 3.

Peak label	Q-measured/Å^{-1}	d spacing/Å	h	l	Q-calculated/Å^{-1}	Deviation/Å^{-1}
1	0.122	51.5	0	1	0.121	− 0.001
2	0.158	39.7	1	0	0.158	0.000
3	0.199	31.6	1	1	0.199	0.000
4	0.241	26.1	0	2	0.242	0.000
5	0.405	15.5	2	2	0.398	− 0.007

(1) The dendrimer units lie in columns perpendicular to the ac plane but with no long range correlation along columns. The in-plane structure has a one dimensional periodicity (along a) and is essentially uniform in the b direction. The lattice parameter is simply related to the position of peak 2.

$$a(\text{rect}) = \frac{2\pi}{Q_2}$$

It seems unlikely that the inter-layer corrections are strong enough to give the rectangular ordering without inducing some periodic ordering along the columns. This possibility is illustrated in figure 6 (*b*) (Col$_{rec}$ mesophase).

(2) The in-plane structure has a two-dimensional periodicity with a high symmetry (e.g. a hexagonal or square net). The higher order peaks from such a structure would be too weak to be observable. The most likely structure for close-packed spheres is hexagonal and we suggest that the $h = 1$, $l = 0$ peak (i.e. peak 2) is actually the $h\ k\ l = 1\ 0\ 0$ peak from a three dimensional hexagonal lattice such as that of the normal smectic-like crystal B phase as illustrated in figure 6 (*c*) (Col$_x$ mesophase). The next peaks in such a lattice (i.e. $h\ k\ l = 1\ 1\ 0$) would be at a $\sqrt{3}$ greater value of Q and are too weak to be seen. This interpretation implies that the lattice parameter a for such a hexagonal lattice is related to the position of peak 2 as follows.

$$a(\text{hex}) = \frac{4\pi}{Q_2\sqrt{3}}$$

which is a factor of $2/\sqrt{3}$ greater than for proposal (1).

There are several reasons for preferring proposal (2) above.

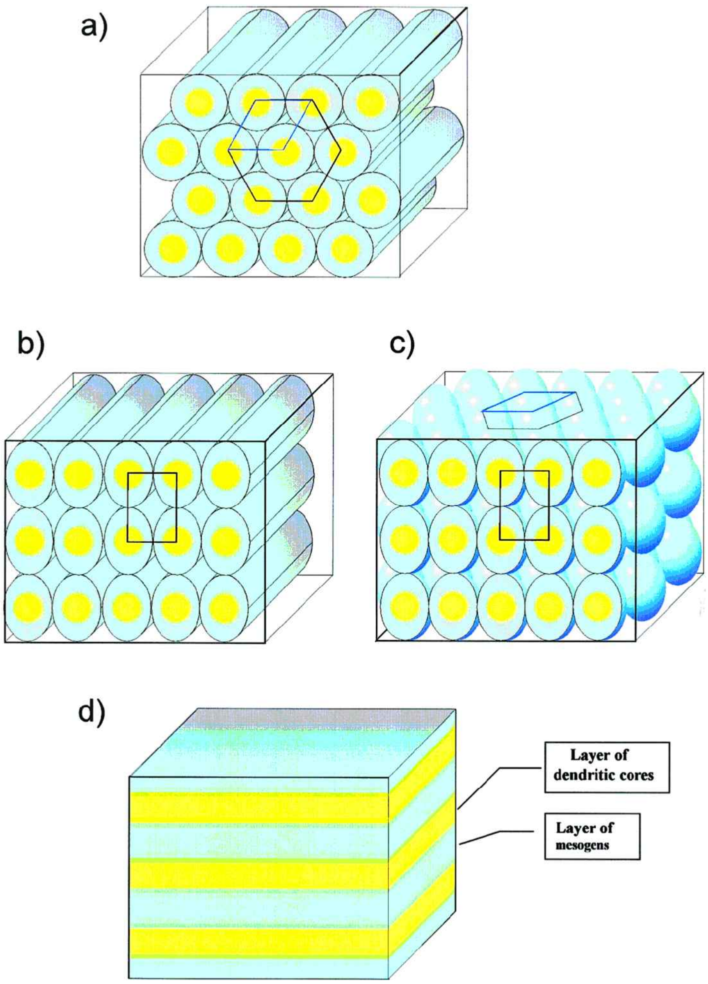


Figure 6. Schematic diagrams of the possible structures of G-5(Und-CB)$_{128}$ consistent with the scattering observed at different temperatures: (*a*) columnar structure with hexagonal ordering of rounded columns (Col$_{hd}$ mesophase); (*b*) columnar structure with rectangular ordering of ellipsoidal columns at 70°C (Col$_r$ mesophase); (*c*) structure with hexagonal lattice of ellipsoidal molecules of LC dendrimer at 70°C (Col$_x$ mesophase); (*d*) lamellar structure (SmA mesophase).

(a) It predicts a reasonable density (1.46 to 1.37 g cm^{-3} as the temperature increases) from the molecular mass divided by the unit cell volume. Proposal (1) cannot be used to predict a density because it does not give a dimension in the second in-plane direction.

(b) The in-plane dimension given by (2) is more consistent with the dimension in the upper phase. In the upper mesophase (121 to 135°C) there is only one slightly broadened peak which remains in the region occupied by peaks 1 to 4. It is at a Q value which extrapolates from 1 0 0 peak in the hexagonal lattice discussed in (2) above and so it is reasonable to suppose that the upper mesophase has a columnar structure with disordered columns and a hexagonal net of columns (Col$_{hd}$ mesophase, figure 6 (*a*)). The columns can move freely parallel to one another and the lamellar characteristics have entirely disappeared. If we accepted proposal (1) above, it would be more difficult to construct a simple model to describe the structural change at 121°C. If the transition were from a two dimensional rectangular lattice to a hexagonal columnar phase, one would expect to see a discontinuity in the Q value at the transition. Very little change is observed which reinforces our preferences for proposal (2).

(c) The molecules are elongated in the c direction and so they will have an ellipsoidal shape with the long axis parallel to the layer normal (on average). It therefore seems unlikely that different interactions will develop in the two in-plane directions as in proposal (1) above. We therefore have a strong preference for proposal (2) for the lower mesophase, although (1) cannot be ruled out with the data currently available.

Taking into account all the X-ray diffraction data and the phase transitions, the structure of the mesophases of the LC dendrimer may be explained as following. First of all let us consider what happens to the molecules when the sample is heated from 30°C. In order to discuss the SAXS results we will consider a single local domain of the structure. At 30°C the smectic A (lamellar) structure exists showing oriented peaks 1 and 4 in the X-ray pattern, figure 6 (*d*). Such a structure assumes the alternation of the layers consisting of mesogenic groups with layers consisting of the carbosilane dendritic cores, figure 7 (*d*). In this case, there is no order within the latter layer. It is uniform because of the softness of the dendritic part of molecules. Short range order within the layers of mesogenic group is seen in the wide angle X-ray scattering (inter-mesogenic distance, about 5 Å), which is consistent with a smectic A mesophase. It is likely that in this phase the dendrimer molecules are significantly elongated along the layer normal direction to maximise the mesogen–mesogen interactions.

Heating of the sample leads to formation of a columnar structure as the dendrimer molecules from adjacent layers form columns so that the mesogenic units can interact more closely. This leads to the realization of the hexagonal or rectangular lattice with the cells described above, figure 6 (*b*, *c*). Since it is formed by a lateral ordering of the dendrimer units, the orientation of the peaks 0 0 1 and 0 0 2 remains parallel in a magnetic field, but the planes 1 0 0 and 1 0 1 appear at intermediate orientations. It can be seen from figure 7 (*a*, *b*, *c*) how the dendrimer molecules may change in elongation. The repeat distance along the planes of columns c becomes equal to the inter-columnar distance within the layers, a(hex), as 120°C is approached. This means that the dendrimer molecules become more spherical as the temperature increases, figure 7 (*a*). This tendency to spherical geometry with increasing temperature is probably responsible for the initial break up of the uniform lamellae at room temperature, because the attractive interactions between mesogens in the same layer are reduced as they become more disordered. The column formation may be driven by the tendency to maximise mesogen–mesogen interactions in adjacent layers as the molecules become less elongated.

Further heating of the sample leads to a loss of the layers as the columns become more mobile and only a rather disordered hexagonal network of columns persists in the upper mesophase, figure 6 (*a*).

Turning to the internal structure of the columns, this seems to be as follows. Each column consists of flattened spherical molecules of LC dendrimers, and all mesogenic groups are located on the surface of the columns only. The inner part of a column consists of the soft dendritic cores of the molecules, figure 7. In the case of the upper mesophase, there are no strong interactions between mesogenic groups and, therefore, they have all orientations in space within the limits of the column's surface, figure 7 (*a*). This leads to the rounded shape of the columns. In the case of the lower mesophase, there are strong interactions between mesogenic groups as evidenced by the rather large enthalpy of the phase transition (2.1 J g^{-1}). This leads to some orientation of the mesogenic groups and is the reason for the elongation of the molecules, figure 7 (*b*, *c*). Further cooling leads to strengthening of inter-mesogenic interactions and, as a result, to a more elongated shape. Finally, this gives rise to a transformation of the columns into lamellae, figure 7 (*d*).

In conclusion, it should be noted that this carbosilane LC dendrimer of the fifth generation with terminal cyanobiphenyl mesogenic groups is the largest LC dendrimer presently known to show mesomorphic properties. It is

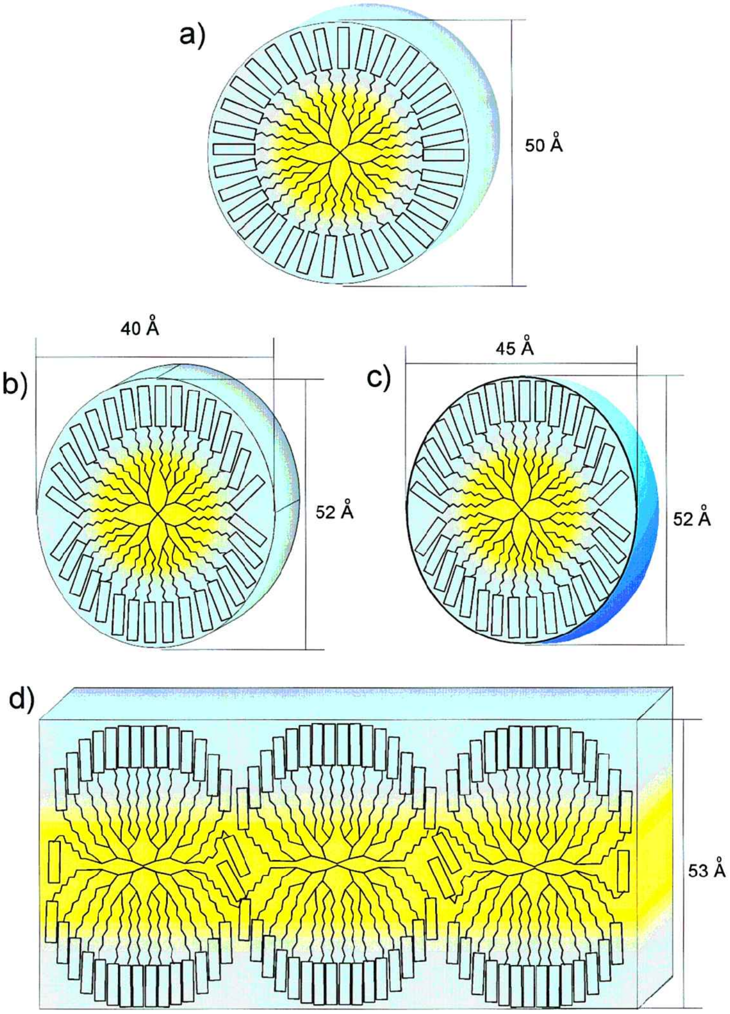


Figure 7. Illustrating the distortion of G-5(Und-CB)$_{128}$ dendrimer molecules in different mesophases: (*a*) rounded shape in Col$_{hd}$ mesophase; (*b*) ellipsoidal shape in Col$_r$ mesophase; (*c*) ellipsoidal shape in Col$_x$ mesophase; (*d*) elongated shape in SmA mesophase.

very different from lower generation LC dendrimers of the same type [3] or having analogous structures [2, 4, 5], which form smectic (lamellar) structures only. It is because the influence of the dendritic core is becoming significant that it forms a columnar mesophase in addition to a lamellar phase.

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References

[1] Percec, V., Chu, P., Ungar, G., and Zhou, J., 1995, *J. Am. chem. Soc.*, **117**, 11 441.

[2] Ponomarenko, S. A., Rebrov, E. A., Boiko, N. I., Vasilenko, N. G., Muzafarov, A. M., Freidzon, Ya. S., and Shibaev, V. P., 1994, *Vysokomol. Soedin., Ser. A*, **36**, 1086 (in Russian); 1994, *Polym. Sci. Ser. A*, **36**, 896 (in English).

[3] Ponomarenko, S. A., Rebrov, E. A., Bobrovsky, A. Yu., Boiko, N. I., Mazafarov, A. M., and Shibaev, V. P., 1996, *Liq. Cryst.*, **21**, 1.

[4] Frey, H., Lorenz, K., and Mülhaupt, R., 1996, *Macromol. Symp.*, **102**, 19.

[5] Lorenz, K., Hölter, D., Stühn, B., Mülhaupt, R., and Frey, H., 1996, *Adv. Mater.*, **8**, 414.

[6] Percec, V., Johansson, G., Ungar, G., and Zhou, J., 1996, *J. Am. chem. Soc.*, **118**, 9855.

[7] Balagurusami, V. S. K., Ungar, G., Percec, V., and Johansson, G., 1997, *J. Am. chem. Soc.*, **119**, 1539.

[8] Ponomarenko, S. A., Rebrov, E. A., Boiko, N. I., Muzafarov, A. M., and Shibaev, V. P., 1998, *Vysokomol. Soedin., Ser. A*, **40** (in the press).

[9] Slaney, A. J., and Goodby, G. W., 1989, *J. mater. Chem.*, **1**, 5.

[10] Ebert, M., Hermenn-Schonherr, O., Wendorff, J., Ringsdorf, H., and Tshirner, P., 1988, *Macromol. Chem., rapid Commun.*, **9**, 455.

[11] Shibaev, V. P., Freidzon, Ya. S., and Kostromin, S. G., 1994, *Liquid Crystalline and Mesomorphic Polymers*, edited by V. Shibaev and Lui Lam (New York: Springer), p. 77.

[12] Tomalia, D. A., and Durst, H. D., 1993, *Top. Curr. Chem.*, **165**, 193.

[13] Newcome, G. R., Moorefield, C. N., and Vögtle, F., 1996, *Dendritic Molecules: Concept, Synthesis, Perspectives* (Weinheim: VCH).

[14] Demus, D., and Richter, L., 1980, *Textures and Liquid Crystals* (Leipzig: VEB Deutsche Verlag fur Grungstoffinustrie), p. 228.