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Carbosilane Liquid Crystalline Dendrimers: From Molecular Architecture to Supramolecular Nanostructures

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ABSTRACT: A systematic study of the influence of generation number on the phase behavior of LC dendrimers is presented. For this purpose, phase behaviors and structures of first to fifth generations of liquid crystalline (LC) carbosilane dendrimers with 8, 16, 32, 64, and 128 terminal cyanobiphenyl groups were investigated. Investigation of thermal behavior of the LC dendrimers by means of polarizing optical microscopy, differential scanning calorimetry, and X-ray diffraction experiments reveals smectic-type mesophases over a wide temperature region. It is shown that with increasing generation number the isotropization temperature increases whereas the enthalpy of this phase transition decreases. The strongest influence of spherical molecular architecture on the phase behavior of the LC dendrimers appears at high generations. In the case of LC dendrimer of the fifth generation, it leads to the formation of two levels of a structural organization. This dendrimer forms different supramolecular nanostructures of columnar type in addition to smectic-like arrangement of mesogenic groups. Possible structures of all mesophases formed are discussed.

Introduction

Currently, there is a growing interest in synthesis and investigation of systems with unusual molecular structure showing mesomorphic properties as evidenced by the growth in papers published in this field. Liquid crystalline (LC) dendrimers are a clear example of such systems. LC dendrimers are a new class of highly branched LC compounds. Their molecules combine structural units capable of LC mesophase formation (mesogenic groups)[1] with dendritic or “cascade” architecture.[2]

Up to now LC dendrimers of different chemistries have been synthesized: polyorganosiloxane,[3] carbosilane,[4] poly(propyleneimine),[5] and poly(amidoamine).[6] Recently the first ferrocene-containing LC dendrimer[7] as well as a ferroelectric LC dendrimer[8] has been reported. All of them were shown to form different smectic mesophases. Dendrimers consisting of mesogenic groups incorporated in each branching point form smectic and nematic mesophases.[9] Some hyperbranched polymers were also shown to be liquid crystalline,[10] but they should be considered as another class of LC compounds. These polymers differ from dendrimers because they have disorder in the arrangement of branching points and do not possess some of the peculiarities of dendrimers.[11] Several dendrimers without mesogenic groups were also shown to be liquid crystalline.[12] However, they have a different origin of the LC mesophase formation.

Depending on the location of mesogenic units in the molecule, two classes of LC dendrimers may be considered.[13] These are LC dendrimers with mesogen-containing branching units[9] and LC dendrimers with terminal mesogenic groups.[3−8] Both LC dendrimers with terminal mesogenic groups and side chain liquid crystalline polymers consist of molecules built up from the following general structural units: polymeric chain, spacer, and terminal (or side chain) mesogenic groups. The main difference between these LC compounds is the different topology of the polymer chain. It is linear in the case of side chain LCPs, while in the case of LC dendrimers it has superbranched, “dendritic” or “cascade” architecture. It should be noted that LC dendrimers are monodisperse compounds. This is another distinction from side-chain LCPs, which are usually polydisperse, as are most synthetic polymers.

It is well-known that all of the structural units forming side chain LCPs influence on the phase behavior of LCPs.[1] For instance, changing the spacer length could give rise not only to the oscillation of the transition temperature (odd/even effect)[14] but also to a change in the mesophase type.[15] An increase of the main-chain length (degree of polymerization) in LCPs leads to an increase of the clearing temperature (T_{Cl}) in the case of low molar weight LC oligomers. However, the effect vanishes in high molar weight LCPs.[16] There is very little information in the literature about the influence of the same structural units on the phase behavior of LC dendrimers with terminal mesogenic groups.

From this point of view, it is very important to establish the main features of their phase behavior including (i) the influence of generation number (responsible for dimensions and molecular weight of dendrimers), (ii) the spacer length between the mesogenic units and the dendritic matrix, and (iii) the chemical nature of the terminal mesogenic groups. The effect of mesogen type on the properties of first-generation LC dendrimers in bulk and in dilute solutions was presented in previous works.[4a,17] Influence of spacer length

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was estimated elsewhere.[5,18] This work presents a systematic study of the role of generation number on the thermal properties of carbosilane LC dendrimers. It was stimulated by the fact that the effect of generation number on mesophase formation has not been clearly distinguished yet.[5a] The only finding was the fact that the temperature range of smectic phases expanded with increases in the generation number of dendritic core.[4d,5b] However, most of the LC dendrimers in question[3−8] form smectic mesophases, which suggests that the dendritic architecture does not reveal its spherical nature. The goals of this work are to show that the spherical molecular architecture of these LC dendrimers does influence their phase behavior and to find how this influence depends on the generation number. For this purpose first to five generations of carbosilane LC dendrimers with cyanobiphenyl (**CB**) terminal mesogenic groups were chosen. Using the same type of mesogenic groups and the same length of aliphatic spacer (**Und** = undecylene) in this series of LC dendrimers allowed the revelation of the influence of generation number on their phase behavior.

Results and Discussion

Synthesis and Characterization. Carbosilane LC dendrimers **G-*n*(Und-CB)*_m_*** of 1, 2, 3, 4, and 5 generations with 8, 16, 32, 64, and 128 terminal cyanobiphenyl mesogenic groups, respectively, were synthesized via a hydrosilylation reaction in toluene in the presence of Pt−catalyst according to Scheme 1.[19] Mesogenic groups were linked to carbosilane dendritic matrixes of the first to fifth generations through an undecylenic spacer in order to facilitate mesophase formation. The structure and purity of all the dendrimers was confirmed by ^{1}H NMR spectroscopy and GPC analysis (see Supporting Information). All LC dendrimers synthesized are monodisperse substances with polydispersity 1.01−1.02. The high purity of these dendrimers was achieved by preparative HPLC. Synthetic details and characterization of this series of LC dendrimers were published elsewhere.[13]

Phase Behavior. The thermal behavior of LC dendrimers was investigated by means of polarizing optical microscopy, differential scanning calorimetry (DSC) in combination with small- and wide-angle X-ray scattering (SAXS and WAXS).

The phase diagram of LC dendrimers **G-*n*(Und-CB)*_m_*** is shown in Figure 1. As can be seen from the data, there are no any significant changes of the phase behavior from the first to third generations. LC dendrimers of the fourth and fifth generations are different from both the previous generations and each other. Let us consider in detail the thermal properties of LC dendrimers of generations 1−3, 4, and 5 in turn.

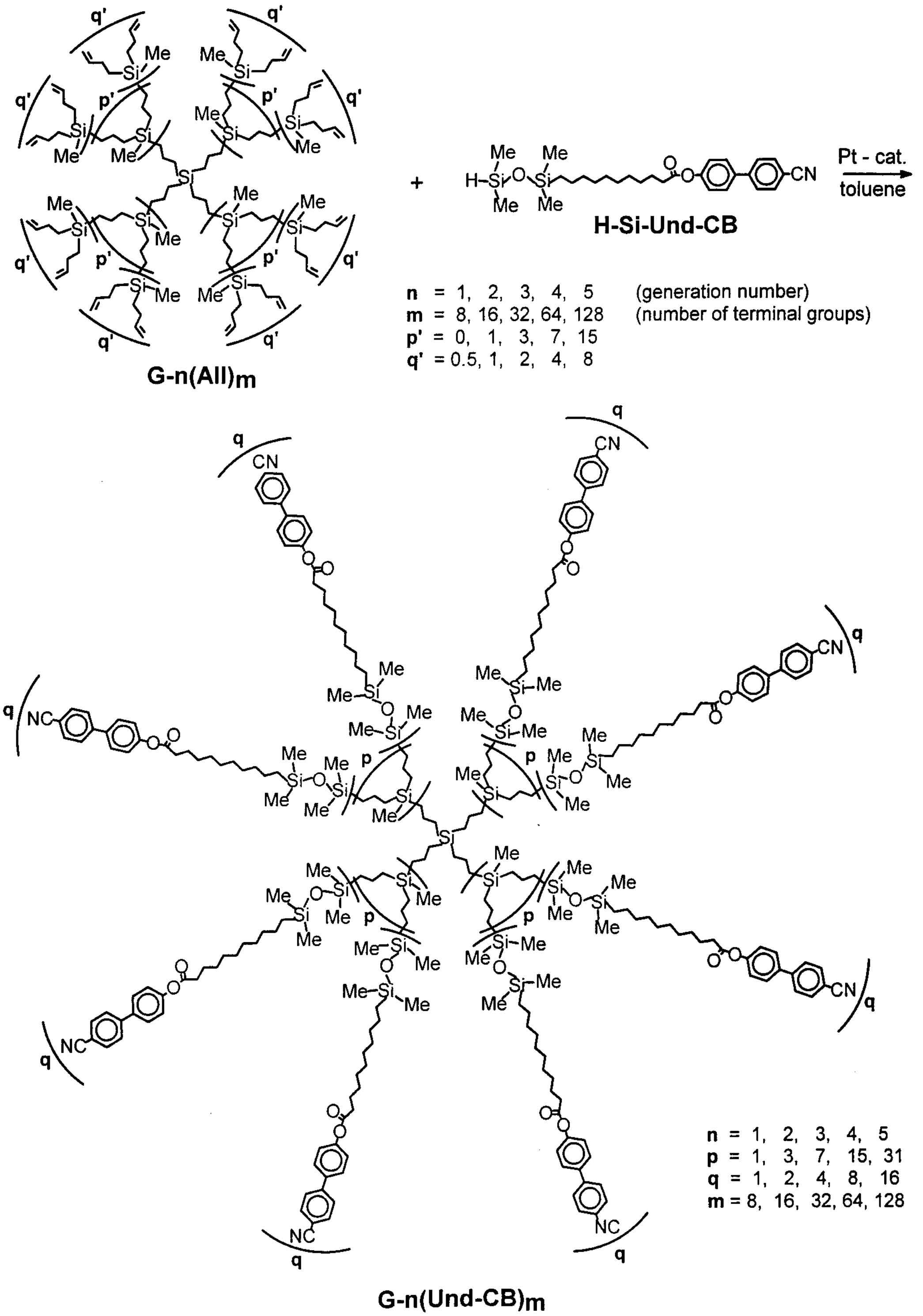
Polarizing optical microscopy showed that the LC dendrimers of generations 1−3 have two different mesophases in the temperature region from room temperature to about 92 °C. Cooling below the clearing point leads to the formation of either a focal conic fan-shaped or a homeotropic texture (Figure 2a) depending on the sample preparation. As known from the literature, both these textures are characteristic of a smectic A (SmA) mesophase.[20] Continuation of cooling until 50−57 °C (a slight dependence on generation number) leads to the following visible changes. The focal conic fan-shaped texture is destroyed by the formation of a broken focal conic fan texture, and the homeotropic texture is transformed into a schlieren one (Figure 2b). According to the literature data, such textural changes correspond to the transition of smectic A mesophase into smectic C (SmC) one. Moreover, this transition is fully reversible, and multiple heating and cooling of the samples of LC dendrimers of generations 1−3 leads to exactly the same textural changes.

DSC showed that the SmC−SmA transition is seen as endothermal peak during heating and exothermal peak during cooling for the third generation of LC dendrimers only (Figure 3). The enthalpy of this transition was 0.6 J/g. Moreover, this peak can be seen not only during the first heating scan but also during cooling and the second heating scan. As for LC dendrimers of the first and second generations, use of samples with rather large masses (about 30 mg) revealed the endothermal peak in the region of the SmC−SmA transition under the first heating scans. Possibly, it is caused by low transition enthalpy (less than 0.3 J/g). Therefore, the enthalpy of the SmC−SmA transition significantly increases when passing from LC dendrimer of the second generation with 16 terminal cyanobiphenyl mesogenic groups to LC dendrimer of the third generation with 32. Turning to the SmA−I transition, it is clearly seen on all heating and cooling DSC scans as a first-order transition, its temperature being in good agreement with the clearing point for all the LC dendrimers.

X-ray measurements in wide and small angle regions confirmed the existence of a smectic mesophase with disordered layers in all the LC dendrimers under consideration, showing two sharp reflections at small angles, corresponding to first- and second-order Bragg reflections from smectic layers, and a diffuse halo at wide angles from the disordered arrangement of mesogenic groups (Figure 4a) for the whole temperature range from room temperature until the clearing point. The corresponding interplanar spacings are presented in Table 1. By comparison of these data with the results received for carbosilane LC dendrimers with methoxyphenyl benzoate mesogenic groups (having the same length of aliphatic spacer),[21] as well as considering the calculated dimensions of cyanobiphenyl mesogenic groups and undecylenic spacer, the following scheme of smectic (lamellae) mesophase was suggested: layers of cyanobiphenyl mesogenic groups alternate with the layers formed by the carbosilane dendritic cores and aliphatic spacers (Figure 5). Cyanobiphenyl mesogenic groups form one-layer packing with partial overlapping of mesogenic groups due to interactions between strong CN-dipoles and easily polarized benzene rings. Such type of the packing is typical for low molar mass alkoxycyanobiphenyls. Similar model was recently suggested for poly(propyleneimine) dendrimers functionalized with cyanobiphenyl mesogenic groups.[5a]

In the region of the SmC−SmA transition (50−57 °C) SAXS measurements showed sudden changes in intensities of the peaks at small angles for all three samples, as well as a small increase (about 0.7−1.2 Å) in the interlayer spacing for **G-2(Und-CB)$_{16}$** and **G-3(Und-CB)$_{32}$** (see Supporting Information) that corresponds to the tilt angle in the SmC mesophase of about 10−12°. These data are in agreement with DSC and polarizing optical microscopy observation of the SmC−SmA transition. Absence of a significant tilt of mesogenic groups or a sharp change in the interlayer spacing for **G-1(Und-CB)$_8$** could be explained by a low tilt SmC mesophase

Scheme 1



(with the tilt angle of mesogenic groups less than 10° respecting to the smectic layers) or by the transition taking place by a change in the azimuthal order of the mesogenic units rather than a change in their tilt angle.[22] In this case, changes of the interlayer spacings during the SmC−SmA phase transition should also be very small (comparable with the experimental error) and could be compensated by the soft dendritic matrix and aliphatic spacers, sandwiched between the layers of mesogenic groups (Figure 5).

Thermal properties of the fourth generation LC dendrimer are different from those of the previous generations. Polarizing optical microscopy showed a focal conic fan-shaped texture, characteristic of the smectic A mesophase, over the whole temperature range up to the clearing point of 109 °C. DSC measurements revealed only one first-order phase transition at a temperature of 109 °C with the enthalpy being 3.7 J/g (Figure 3). It corresponds to the transition from the smectic A mesophase to the isotropic melt. X-ray measurements are in accordance with these results. Two small angle reflections corresponding to first- and second-order Bragg reflections from smectic layers as well as a diffuse reflection in the wide-angle region are present on the

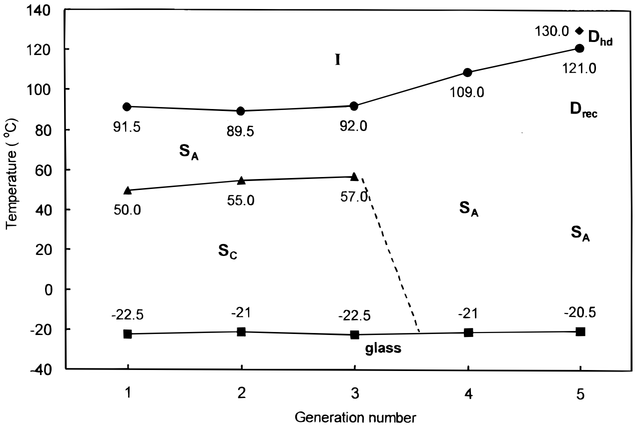


Figure 1. Phase diagram of LC dendrimers **G-*n*(Und-CB)*m*** ($n = 1-5$, $m = 8-128$).

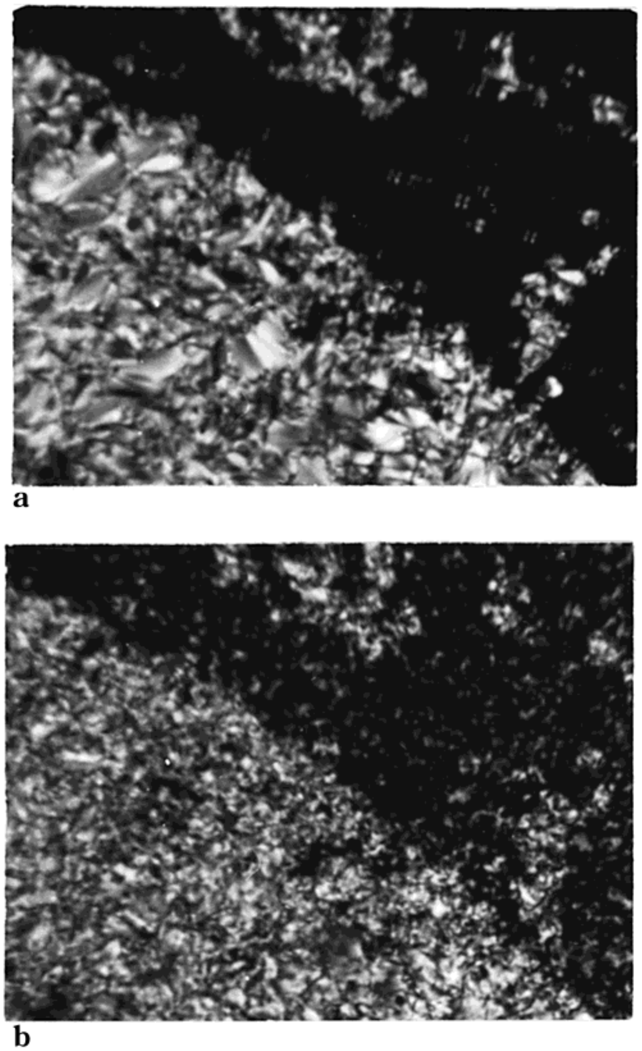


Figure 2. Optical polarizing photomicrographs of characteristic textures of LC dendrimers (field of view 300 × 400 nm): (a) focal conic fan-shaped texture of **G-2(Und-CB)$_{16}$** (SmA, 64 °C, thin sample); (b) broken fan-shaped texture of **G-2(Und-CB)$_{16}$** (SmC, 35 °C, the same spot as in a).

X-ray pattern until clearing temperature (Figure 4b). Therefore, increasing the generation number from 3 to 4 and consequently changing of the number of terminal groups from 32 to 64 leads to a significant increase of the clearing temperature (by 17 °C). In addition, the smectic C mesophase disappears in this generation.

Passing to the LC dendrimer of the fifth generation, containing 128 terminal cyanobiphenyl mesogenic groups, gives rise to more noticeable changes of the thermal behavior in comparison with previous generations. Polarizing optical microscopy shows three different textures depending on the temperature (Figure 6). In the region of 70−119 °C, a bright colorful mosaic texture is observed (Figure 6a). When the sample is cooled below 70 °C, the mosaic texture is gradually destroyed (Figure 6b). On heating of the mosaic texture until 119 °C, it becomes almost isotropic. Further heating leads to the formation of another weak birefringent mosaic texture, annealing of which shows “dendritic” internal structure inside each domain (Figure 6c), which transforms into the isotropic melt at 135 °C. Similar textures were observed for hexagonal columnar mesophase[23a] and the so-called M_x phase.[23b] DSC measurements are in accordance with the polarizing optical microscopy data. The DSC curve shows two first-order phase transitions: one peak at 121 °C with an enthalpy of 2.2 J/g and another peak at 130 °C with an enthalpy of 0.2 J/g (Figure 3).

It is well-known from the literature, that mosaic textures are characteristic of ordered smectic[20] and columnar mesophases.[23,24] It indicates that some elements of further ordering within the smectic layers are present in the phase. In other words, it means that mosaic texture is characteristic of structures that are more ordered than smectic A or smectic C mesophases. X-ray measurements confirmed these observations.

Structure of G-5(Und-CB)$_{128}$ Mesophases. The small-angle X-ray scattering (SAXS) from an unaligned sample of **G-5(Und-CB)$_{128}$** showed from two to six Bragg reflections at different temperatures. They could be indexed as (001), (100), (101), (002), (200), and (201) from a 2D rectangular unit cell (Table 2, Figure 7a). It is noteworthy that this LC dendrimer shows an unexpected increase in order when heating as is strongly evidenced by SANS measurements.[25] At 30 °C, only peaks 001 and 002 are seen and their Q values increase with the temperature.[26] Their intensities decrease with increasing temperature and they disappear completely at 121 °C. Peaks 100 and 101 appear only above 40 °C, and they exist until the transition at 121 °C. Peak 100 persists above the transition although it is slightly broader and weaker. No significant change of this peak was observed at the temperature corresponding to the transition to the isotropic phase. The intensities of peaks 100 and 101 are much weaker then the intensity of peak 001 and they have different temperature dependencies. The position of peak 100 is shifted to the lower Q with increasing temperature while peak 101 is temperature independent, that is in agreement with 2D rectangular unit cell, whose dimensions (a, in-plane, and c, the layer spacing) vary with temperature as shown in Figure 7b. Peaks 200 and 201 was possible to detect using only a more intense synchrotron X-ray beam and higher resolution detector (Figure 7a). X-ray reflections at 101 °C and their indexing for the rectangular unit cell are presented in Table 2. This finding allowed to distinguish between 2D rectangular and 3D hexagonal unit cells, both of them were previously suggested for this LC dendrimers on the base of usual (Cu Kα) radiation.[25,27]

WAXS measurements showed a diffuse halo at $Q = 1.15-1.20$ Å^{-1} for the temperature region 30−121 °C. It corresponds to the lateral spacing of about 5.3 Å

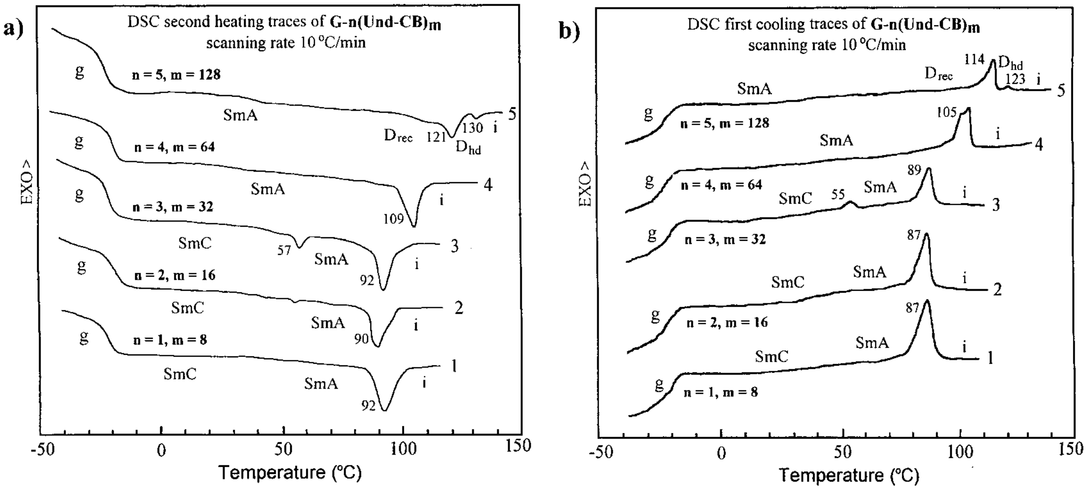


Figure 3. Second heating (a) and first cooling (b) traces of LC dendrimers **G-*n*(Und-CB)*m***: (1) **G-1(Und-CB)$_8$**; (2) **G-2(Und-CB)$_{16}$**; (3) **G-3(Und-CB)$_{32}$**; (4) **G-4(Und-CB)$_{64}$**; (5) **G-5(Und-CB)$_{128}$**.

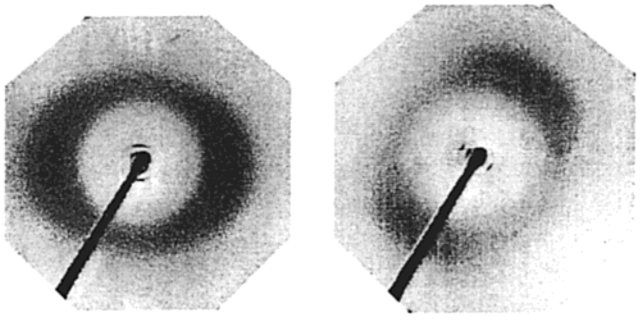

(a) (b)

Figure 4. X-ray diffraction patterns: (a) **G-3(Und-CB)$_{32}$**, 70 °C, smectic A; (b) **G-4(Und-CB)$_{64}$**, 36 °C, smectic A.

Table 1. Interplanar Spacings[a] at 30 °C for LC Dendrimers G-*n*(Und-CB)*m*

LC dendrimer	layer spacing (Å)	intermesogenic distance (Å)
G-1(Und-CB)$_8$	47.3 ± 0.5	4.8
G-2(Und-CB)$_{16}$	47.3 ± 0.3	4.8
G-3(Und-CB)$_{32}$	48.6 ± 0.3	4.8
G-4(Und-CB)$_{64}$	50.8 ± 0.3	4.6
G-5(Und-CB)$_{128}$	53.0 ± 0.3	5.3

[a] Note. Interplanar spacing does not greatly change with increasing temperature almost until the clearing point for LC dendrimers first to fourth generations (see Supporting Information). Changes of the interplanar spacings for **G-5(Und-CB)$_{128}$** are shown in Figure 7b.

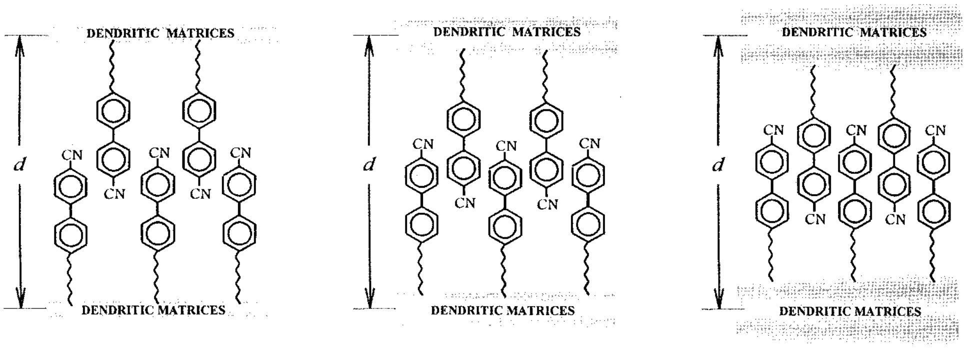
which is typical of phases such as smectic A formed by calamitic molecules.

On the basis of the structural data the following structural models of mesophases formed by LC dendrimer **G-5(Und-CB)$_{128}$** are suggested. At 30 °C, the smectic A (lamellar) structure exists, assuming the alternation of the layers consisting of mesogenic groups with layers consisting of the carbosilane dendritic cores (Figure 8a). In this case, there is no order within the dendritic layers. They are amorphous due to "softness" of the dendritic part of molecules. At the same time there is a short-range order within the layers of mesogenic group 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 maximize the mesogen−mesogen interactions (insertion in Figure 8a).

Heating the sample leads to gradual formation of a columnar supramolecular structure in the dendritic layers as a rectangular columnar mesophase D_{rec} (Figure 8b), which appears as several additional reflections on the X-ray pattern indexed as (100), (101), (200), (201), and (202) of the 2D rectangular cell. Parameters of this cell depend on the temperature: increasing of the temperature leads to increase of parameter *a* (in the layer plain), but decrease of parameter *c* (interlayer distance) (Figure 7b). It can be explained by the following: under increase of the temperature molecules of LC dendrimers become less elongated and their shape become more spherical that is favored to formation of ellipsoidal columns (Figure 8b). Each column consists of ellipsoidal molecules of LC dendrimers, flattened to a direction of a columnar axis and elongated perpendicular to it (like shish-kebab). All mesogenic groups are located on the surface of the columns only while the inner part of the column consists of soft dendritic cores of the molecules of LC dendrimers.

Further heating leads to a loss of the layers as the columns become more rounded and only a rather disordered hexagonal network of columns persists in the upper mesophase above 121 °C (Figure 8c). It is formed by rounded columns; each of them consists of spherical molecules of LC dendrimers, flattened parallel to the columnar axis. In this mesophase strong orienting interactions between mesogenic groups are absent and this structure is formed only by the whole molecules of LC dendrimer owing to microphase separation between the aliphatic dendritic part of the molecules and the aromatic mesogenic groups. It is confirmed by a rather large enthalpy of the D_{rec}−D_{hd} phase transition (2.1 J/g), while the enthalpy of the transition D_{hd}−I is significantly less (0.2 J/g). It is some kind of intramolecular phase separation. That is why carbosilane LC dendrimers can be named as a new type of intramolecular phase-separated and self-assembled nanostructure materials.[28]

Turning to the fact that peaks 001 and 002 get weaker with temperature increasing while peaks 100 and 101 become stronger seems to suggest an alternative explanation of the structure between 40 and 121 °C: the coexistence over a broad temperature range of two different structures, one characterized by peaks 001 and 002 and the other by peaks 100 and 101 (Figure 7a). This would be a good explanation if we see only changes in the peak intensities with the temperature. However,



G-1 G-2 G-3

Figure 5. Scheme of packing of cyanobiphenyl mesogenic groups in the smectic layer for low generations of LC dendrimers.

there are also gradual changes in the *Q* values of these peaks, which are interconnected each other as was shown above. It means that these two structures should strongly influence each other and, consequently, they are not independent. That is why the explanation with one structure (D_{rec}) with only two temperature-dependent parameters in the region of 40−121 °C is more preferable to considering the coexistence of two structures. The fact that no any sharp transition from SmA to the D_{rec} mesophase is seen either by SAXS or by DSC could be explained as follows. Actually structural parameters of the lamellar mesophase becomes a part of the structure of the D_{rec} mesophase, while the latter is gradually formed inside the smectic layers as a higher level of structural organization or as a superstructure of LC dendrimers. It means that there are no sharp changes in the structure during this phase transition, as well as it does not lead to any sharp changes in the heat flow in the DSC. In this sense it is better to say that two levels of structural organization in D_{rec} mesophase coexist: smectic layers due to interaction between mesogenic groups and columnar arrangement of LC dendrimer molecules of as a whole. As opposite to this, there is only one level of structural organization in each of the other mesophases: arrangement of mesogenic groups in the low temperature (SmA) mesophase or supramolecular assembling of molecules of LC dendrimer in the high-temperature (D_{hd}) mesophase. This conclusion as well as structural models suggested above were confirmed using SANS measurement from a pre-aligned sample in a 9.4 T magnetic field. Although the orientation was not very good, it was shown that only peaks 001 and 002 tend to align, while the other peaks did not align. It correspond to alignment of smectic layers formed by cyanobiphenyl mesogenic groups, while the columns formed by dendritic molecules as a whole did not align.

It should be noted that the hexagonal columnar arrangement of dendritic molecules was found recently for third generation carbosilane dendrimer with perfluoroalkyl end groups.[29] It was proposed that the dendrimer organized into rows of stacked molecules, with the perfluorinated surface of the constituent dendrons pointing outward.

Influence of Generation Number on the Phase Behavior. Let us come back to the phase diagram of LC dendrimers (Figure 1). The following is noteworthy. First, the glass transition temperature remains practically constant with increasing generation number within the limits of experimental uncertainties. This means that the temperature of the glass transition of LC dendrimers represents the freezing of translational and rotational motion of terminal groups. Second, both the temperature and the enthalpy of the SmC−SmA transition increase with increasing generation number from generation one to generation three. The temperature of the SmA−I transition does not vary significantly for the first three generations, and the enthalpy of this transition decreases (Figures 1 and 9). It is possible to explain such a phase behavior by interactions of two opposite factors. On one hand, the number of terminal mesogenic groups per molecule of LC dendrimer grows with increasing generation number. This leads to amplification of cooperative interaction of these groups. As a result, the temperature of SmC−SmA transition increases. On the other hand, with increasing generation number the size and the “crowding” of mesogenic groups on the surface of LC dendrimer molecules also increase, and their shape becomes more and more spherical. It opposes the ordering of mesogenic groups into smectic layers and reduces the anisotropy of system. As a result, the enthalpy of SmA−I transition decreases. The temperature of this transition is practically the same for the first to the third generation that is possibly due to the influence of these two factors appear to be opposed. With further increase of generation number, the transition temperature increases and the enthalpy decreases in general. Thus, from the above-stated consideration, it is possible to reveal the following two opposite tendencies, which take place with the increase of the generation number. One is the increase of temperatures of the phase transitions because of the strengthening cooperative interactions of the increasing number of terminal mesogenic groups. The second is a decrease of the enthalpy of phase transitions because molecules of the LC dendrimer become more and more rigid and their shape comes nearer to spherical. Finally, it results in the appearance of new, unusual supramolecular structures of columnar types on the fifth generation.

It is necessary to note that the values of enthalpy of SmA−I transition for LC dendrimers (5.7−2.1 J/g) are significantly lower than ones typical for the same transition in low molar mass liquid crystals (for example, 11.0 J/g for a monomer **H−Si−Und-CB**). Let us consider a more detailed dependence of the SmA−I transition enthalpy on generation number for LC dendrimers **G-*n*(Und-CB)*m*** (Figure 9). To estimate the contribution from each mesogenic group, not only the direct experimental data expressed in J/g but also calculated values of enthalpies expressed in kJ/(mol of

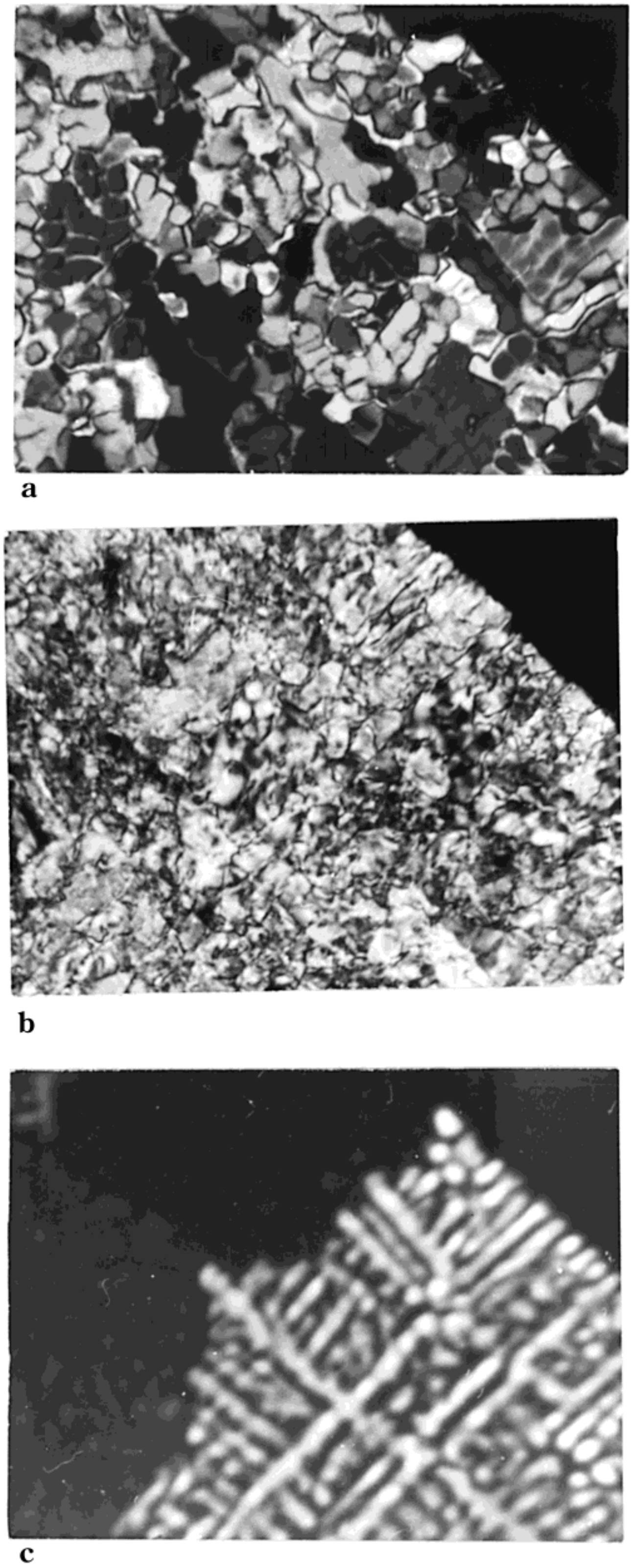


Figure 6. Optical polarizing photomicrographs of characteristic textures of LC dendrimer of fifth generation **G-5(Und-CB)$_{128}$** (magnification ×180): (a) colorful mosaic texture at 113 °C; (b) "broken" mosaic texture at $T = 40$ °C; (c) mosaic texture of the upper phase annealed at $T = 124$ °C during 2 h.

Table 2. *Q* Values Measured from G-5(Und-CB)$_{128}$ at Different Temperatures

temp/°C	indexing: *hkl*	*Q* measd/Å^{-1}	*Q* calcd/Å^{-1}	dev/Å^{-1}	*d* spacing/Å
30	001	0.115			54.6
	002	0.230			27.3
70[a]	001	0.122	0.121	−0.001	51.5
	100	0.158	0.158	0.000	39.7
	101	0.199	0.199	0.000	31.6
	002	0.241	0.242	0.000	26.1
	202	0.405	0.398	−0.007	15.5
101[b]	001	0.1265	0.1269	−0.0003	49.53
	100	0.1504	0.1505	−0.0001	41.75
	101	0.1969	0.1968	0.0001	31.92
	002	0.2537	0.2537	0.0000	24.77
	200	0.2926	0.3009	−0.0083	20.89
	201	0.3296	0.3266	0.0030	19.24

[a] Calculated for a rectangular unit cell with a(rect) = 39.7 Å and c = 52.0 Å. [b] Calculated for a rectangular unit cell with a(rect) = 41.75 Å and c = 49.53 Å.

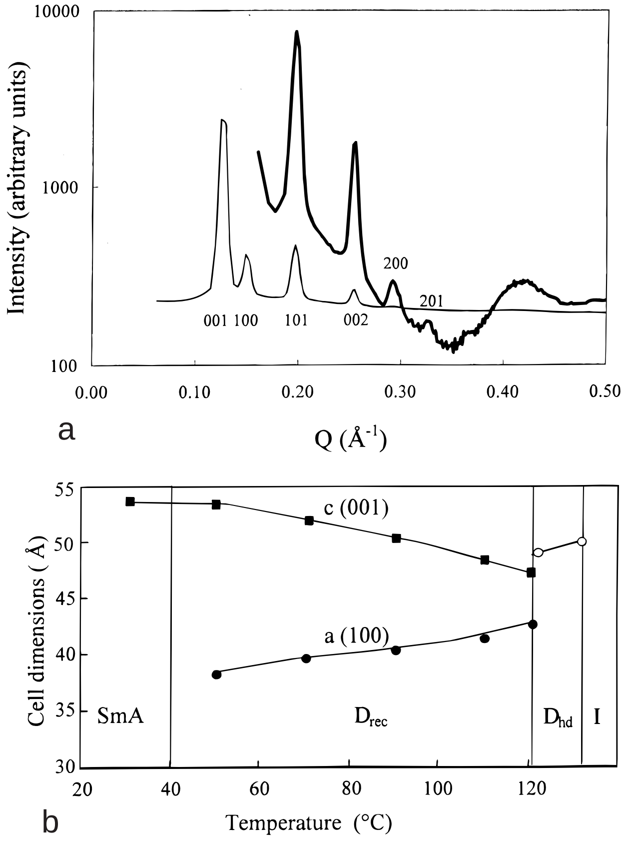


Figure 7. (a) X-ray diffraction from **G-5(Und-CB)$_{128}$** at 101 °C (thin line, low intensity; thick line, high intensity with the strongest reflections filtered). (b) Temperature dependence of the lattice parameters for D$_{rec}$ and D$_{hd}$ unit cells of **G-5(Und-CB)$_{128}$**.

mesogenic groups) are shown in the figure. As it is seen from the data presented, such recalculation did not result in any qualitative changes of the dependence. For both curves, the nonlinear decrease of the enthalpy of transition is observed with increase of generation number. As was already discussed above, such a tendency is explained by the increasing rigidity of dendrimer molecules, resulting in more spherical shapes of the molecules, hindering smectic ordering of terminal mesogenic groups. Unexpectedly, the LC dendrimer of the fourth generation has a larger value of the enthalpy in comparison with the LC dendrimer of generation 3. This deviation from the trend could be explained by the change of packing type of cyanobiphenyl mesogenic groups in a mesophase. It is known from the literature that two types of packing of cyanobiphenyl mesogenic

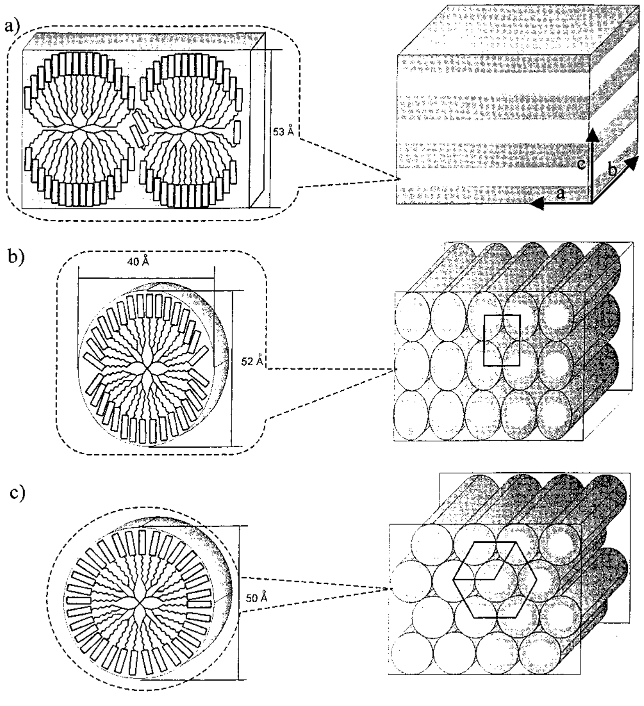


Figure 8. Models of structures formed by LC dendrimer **G-5(Und-CB)$_{128}$** at different temperatures: (a) lamellar structure (SmA mesophase 40 °C). (b) Columnar structure with rectangular ordering of ellipsoidal columns (D_{rec} mesophase, 70 °C). (c) Columnar structure with hexagonal ordering of rounded columns (D_{hd} mesophase, 130 °C). Insertions: the proposed shape of the **G-5(Und-CB)$_{128}$** molecule in different mesophases.

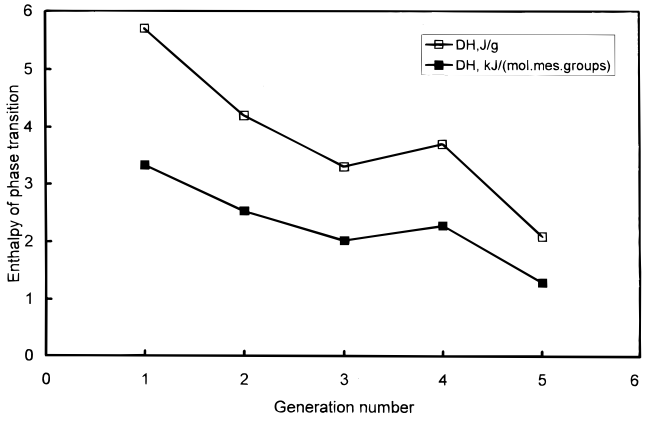


Figure 9. Dependence of enthalpy on the SmA–I phase transition from generation number.

groups are possible: one-layer packing with an overlapping of mesogenic groups and two-layer packing without an overlap.[30] As follows from our earlier results, the one-layered packing with an overlapping of mesogenic groups is realized for the LC dendrimer of the first generation with cyanobiphenyl mesogenic groups.[4a] With increasing generation number the amount of terminal mesogenic groups grows in a geometrical progression (8, 16, 32, 64, and 128 for generations 1, 2, 3, 4, and 5, respectively), while the radius of a molecule grows slower (on a square-law dependence). Therefore, the density of a surface layer of molecule consisting of cyanobiphenyl groups is increased. Consequently, the free volume per each mesogenic group decreases. It can lead to a change in packing of terminal mesogenic groups from one-layered into two-layered packing for some generations of LC dendrimers. Probably, it happens for the LC dendrimer of generation 4. The idea of a change in the overlap of the mesogenic units as the generation number increases is supported by the layer spacing reported in Table 1 that shows different trends for low and high generation numbers. The change in packing could result in a small energy gain and consequently in a deviation from the tendency considered above.

Despite the increase of rigidity of LC dendrimer molecules with increasing generation number, LC mesophases are observed over a wide temperature interval even for the fifth generation with 128 terminal mesogenic groups. At the present time, it is the largest generation of LC dendrimer with terminal mesogenic groups showing mesomorphic properties. Probably, this is promoted by the structure of the surface layer of the dendrimer molecule, namely by the presence of long spacers $-\mathrm{Si(CH_3)_2OSi(CH_3)_2(CH_2)_{10}{-}OOC}-$, by which the terminal mesogenic groups are attached to the carbosilane dendritic cores. In the literature, the synthesis of dendrimers containing 36 and 108 terminal cholesteryl groups, linked to carbosilane dendrimers of a similar structure directly (without a spacer) has been described.[18] However, neither of these compounds display liquid crystal properties (i.e., they have no birefringence) probably because of the absence of a spacer. The behavior of such dendrimers with terminal mesogenic groups is reminiscent of features in comb-shaped LC polymers. It is known, for the latter, that in the case of direct connection of mesogenic groups to a polymeric chain they are amorphous. Only the presence of spacers between mesogenic groups and the main polymeric chain results in formation of liquid crystal mesophases.[31] It is also necessary to take into account the influence of the siloxane present in a spacer. The unique flexibility of the group $-\mathrm{(CH_3)_2Si{-}O{-}Si(CH_3)_2}-$ is known from the literature.[32]

Conclusions. Phase behaviors and structures of five generations of carbosilane LC dendrimers with cyanobiphenyl mesogenic groups were considered. The influence of the generation number on the phase behavior of these systems having unusual molecular architecture was investigated. It was shown that for the lower generations the influence of the dendritic architecture is very restricted. The first to fourth generations of these LC dendrimers form lamellar (smectic A and C) mesophases only. Nevertheless, increasing generation number leads to more rigid and spherical dendritic molecules that do not favor smectic mesophase formation, and the enthalpy of the SmA–I transition decreased. Finally, the fifth generation of LC dendrimer forms not only lamellar but also supramolecular columnar nanostructures. Such superstructures include two levels of molecular organization. One is a smectic-like arrangement of the mesogenic groups and the other one is self-assembly of molecules of LC dendrimers in a columnar-type nanostructure. In this work, an undecylene spacer between the dendritic core and mesogenic groups was used, and this leads to the realization of supramolecular structures only in the fifth generation. Possibly, such superstructures could be formed in lower generations also if shorter spacer were used. This work is in progress now. We will investigate whether this type of supramolecular ordering is common for LC dendrimers and potential applications of such new LC nanostructures in smart molecular devices in future work.

Experimental Section

Materials. 4′-Cyanobiphenyl-11-(tetramethyldisiloxy) undecanoate (**H−Si−Und-CB**) was prepared according to the scheme described before.[4a] Toluene was dried by refluxing over Na and was distilled before use. THF was refluxed over NaOH and freshly distilled before use. All other solvents were distilled before use. All other chemicals were commercially available and used as received.

Methods. GPC analysis was performed in THF on a Knauer setup equipped with an Ultrastyragel 8 × 300 mm column (Waters) having pore size 10^3 Å and the following detectors: RI Waters R-410 and UV spectrometer Knauer. All data are referenced to narrow polystyrene standards. A Vertex 32 × 250 mm column fulfilled with Eurospher Si-100 (7 μm) was used for preparative HPLC. A Waters 19 × 300 mm column filled with Ultrastyragel, 10^3 Å, was used for preparative GPC. Phase transitions were studied by differential scanning calorimetry (DSC) with a Mettler TA-4000 thermosystem at a scanning rate of 10 °C/min. Sample weights were typically chosen between 12 and 25 mg. The polarizing microscopic investigations were performed using a Mettler FP-800 central processor equipped with a hot stage Mettler FP-82 and control unit in conjunction with a Lomo R-112 polarizing microscope. X-ray diffraction measurements were made at Bristol University using Cu Kα radiation ($\lambda = 1.542$ Å) from a 1.2 kV sealed tube. Monochromatization was done with a graphite crystal and the diffraction pattern collected using a two-dimensional position-sensitive detector equipped with a computer. All samples were preoriented in a 9.4 T magnetic field by cooling from the isotropic state to 20 °C at a rate of 0.5 °C/min. Further high-resolution measurements were made at the ESRF, Grenoble, France, using the ID2A beamline. A wavelength of 0.7 Å and a CCD detector were used.

Synthesis. Synthesis and characterization of all the dendrimers both with allyl and cyanobiphenyl terminal groups was performed according to the technique published elsewhere.[13]

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Supporting Information Available: Figures showing GPC traces of carbosilane dendrimers of the terminal cyanobiphenyl mesogenic groups **G-*n*(Und-CB)**$_m$ ($n = 1-5$, $m = 8-128$) and the temperature dependence of SAXS data for **G-*n*(Und-CB)**$_m$ ($n = 1-4$, $m = 8-64$). This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Q is the scattering vector ($Q = 4\pi^*\sin(\vartheta)/\lambda$), where 2ϑ is the scattering angle and λ is the wavelength.

(27) In that case, the rectangular 2-D cell was considered as a constituent part of the 3-D hexagonal cell. See ref 25.

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