PAMAM- and DAB-Derived Dendromesogens: The Plastic Supermolecules

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Two families of liquid crystal dendrimers consisting of a dendrimeric core [fourth and fifth generations of poly(amidoamine) (PAMAM) and poly(propyleneimine) (DAB)] and several large-sized mesogenic units (incorporating three, six, and nine terminal alkoxy chains) have been prepared. The study of these materials reveals the existence of a hexagonal columnar mesomorphism in all cases. We propose a model to explain this behavior based on theoretical calculations made from experimental X-ray diffraction data. The plasticity of the dendrimeric cores, related to their conformational freedom, allows the macromolecules to adopt a cylindrical shape in which the mesogenic units are accommodated around the central core. As a result of this cylindrical symmetry of the molecules, a supramolecular columnar arrangement is present in the mesophase. A complete degree of functionalization of some of the dendrimers would prevent the appearance of a columnar mesophase according to our model. However, we have found that, in all cases, the number of promesogenic units attached to the dendrimer cores is lower than that possible, which permits the cylindrical arrangement of the macromolecules and the existence of columnar mesomorphism.

Introduction

Dendrimers as practically monodisperse and well-defined polymeric materials offer interesting opportunities in materials science.[1] In recent years, the use of dendrimers as building blocks for the construction of supramolecular architectures has attracted the interest of many researchers. As a result, a great variety of materials combining the presence of both a dendritic moiety and different functionalities within the macromolecular architecture have been reported.[2]

Correlations between molecular morphology and macroscopic packing constitute, to a certain extent, an important factor in the study of self-organizing materials, from both a fundamental and a practical point of view;[3] although, in some cases, the predictions of mesophases and molecular aggregates based on geometrical considerations have failed.[4] It is well-known that the conformation of branched dendrimers evolves from an open, extended form to a globular shape as the generation number increases,[5] until the so-called "de Genne dense packing" state is reached.[6] X-ray and small-angle neutron scattering experiments have shown that the higher generations of poly(amidoamine) (PAMAM) and poly(propyleneimine) (DAB) dendrimers have a spherical shape.[7] The covalent linkage of certain groups to the dendrimeric skeleton in order to obtain functionalized materials, that is, liquid crystal dendrimers, causes the modification of the molecular conformation and, therefore, the occurrence of a completely different macroscopic packing.

Dendrimeric liquid crystals can be considered as a group of liquid-crystalline, high-molecular-weight compounds and can be achieved with a shape-persistent, disklike skeleton,[8]

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by using benzyl ether units as branch junctures[9] or by functionalizing the dendrimer periphery with mesogenic units.[10]

In recent years, we have reported on the mesomorphic properties of a series of liquid crystal dendrimers prepared by the latter strategy mentioned above.[11−18] These investigations have allowed us to establish molecular and mesophase models to explain the mesomorphic behavior of the dendrimeric systems, and these have proven to be adequate tools for the study of the relationship between the molecular structure and the mesomorphic activity. Liquid crystal dendrimers can be considered as block molecules, in analogy to block copolymers, since they are made up of at least two incompatible parts, the dendritic core and the terminal groups, and therefore, a microphase-separated structure is favored.[19] The central starburst polymer leads to a spherical disordered arrangement (entropic contribution), while the mesogenic terminal units tend to interact with each other, giving rise to the liquid crystal state (enthalpic contribution). The mesomorphic properties will depend on the enthalpy−entropy balance, the degree of chemical incompatibility, and the size of the different building blocks as well as the structure of the mesomorphic unit. We have functionalized the commercially available dendrimers PAMAM and DAB with different (pro)mesogenic units and studied the influence of this structural variation on the mesomorphic behavior of the dendrimers. As a result, we have obtained materials which exhibit nematic,[15] lamellar,[11,12,17,18] and columnar[13,16,18] mesophases depending on the structure of the mesogenic unit attached to the dendrimers (PAMAM or DAB), which have the ability to adopt the conformation leading to the most stable molecular arrangement in the mesophase.

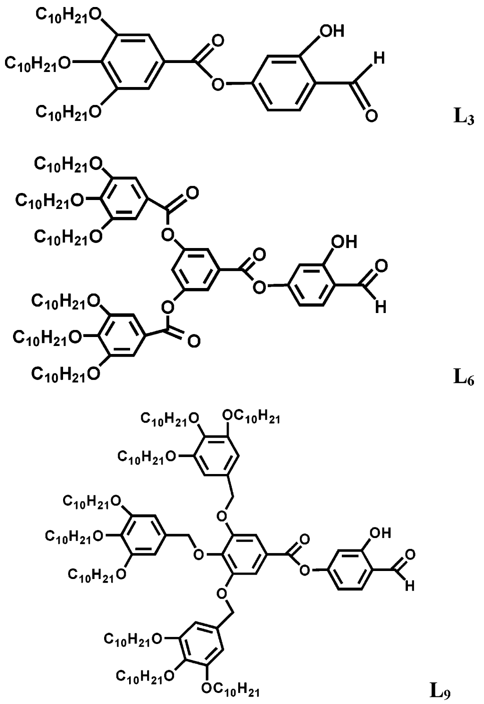

Figure 1. Chemical structures of the promesogenic units connected to DAB and PAMAM dendrimers.

To further investigate the influence of the structure of the (pro)mesogenic units in the mesomorphic behavior of the dendrimeric materials, we have introduced bulky units at the periphery of the fourth and fifth generations of amino-terminated PAMAM and DAB [PAMAM(NH$_2$)x, DAB-(NH$_2$)x, with $x = 32$ and 64], with the aim of achieving cubic mesophases, since we thought that the increased volume around the dendritic core would force the dendrimer to adopt a globular conformation. Three promesogenic units have been selected, bearing three, six, and nine terminal chains (see Figure 1).

However, the study of the dendrimers prepared has revealed, in all cases, the existence of a thermotropic hexagonal columnar mesophase. This fact is explained because the complete functionalization of the dendrimers has not been achieved, and as a consequence, the dendritic scaffold is flexible enough to adopt a conformation that allows the accommodation of the bulky mesogenic units within a columnar supramolecular arrangement.

Results and Discussion

Synthesis and Characterization. The dendrimers were synthesized by the condensation of the aldehydes (L_3, L_6, and L_9) with the terminal amino groups of the corresponding

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Table 1. MALDI−TOF Molecular Weights; GPC Polydispersity Indices of the Dendrimers; Average Number of Mesogenic Units Per Dendrimer; Calculations of the Surface, Diameter, and Height of the Model Cylinders for the Dendrimer Molecules Taking into Account the Experimental Molecular Weight Values

dendrimer	M_w	PDI	mesogenic units	degree functionalization	T (°C)	d_{exp}	S_d[a]	ϕ_d[a]	h_d[a]	S_m[b]	ϕ_m[b]	h_m[b]
PAMAM(L_3)32	23 802	1.14	24	0.75	60	55.8	3595	67.7	11.0	1043.5	36.5	11.0
DAB(L_3)32	20 096	1.31	24	0.75	40	44.4	2276	53.8	14.7	396.5	22.5	14.7
PAMAM(L_3)64	46 133	1.92	46	0.72	80	56.2	3647	68.1	21.0	1123.8	37.8	21.0
DAB(L_3)64	36 268	1.94	42	0.66	50	47.3	2583	57.3	23.3	505.1	25.4	23.3
PAMAM(L_6)32	31 150	1.44	17	0.53	25	48.6	2727	58.9	19.0	604.8	27.8	19.0
DAB(L_6)32	41 778	1.51	27	0.84	25	43.6	2195	52.9	31.6	183.9	15.3	31.6
PAMAM(L_6)64	60 839	1.69	33	0.52	25	51.6	3074	62.6	32.9	718.2	30.2	32.9
DAB(L_6)64	47 529	1.83	29	0.45	25	44.6	2296	54.1	34.4	342.6	20.9	34.4
PAMAM(L_9)32	61 554	1.17	28	0.87	50	51.4	3050	62.3	33.5	342.3	20.9	33.5
DAB(L_9)32	44 937	1.17	21	0.66	80	43.1	2145	52.3	34.8	167.1	14.6	34.8
PAMAM(L_9)64	97 967	1.26	43	0.67	80	51.4	3050	62.3	53.3	442.6	23.7	53.3
DAB(L_9)64	78 066	1.25	36	0.56	80	47.9	2649	58.1	48.9	240.7	17.5	48.9

[a] Molecular weight and volume of the dendrimer; surface, diameter, and height corresponding to the dendrimer cylinder. [b] Molecular weight and volume of the dendritic matrix; surface, diameter, and height corresponding to the dendritic matrix subcylinder.

generation of PAMAM or DAB.[11] All the compounds are soluble in solvents such as dichloromethane, chloroform, and THF and are insoluble in ethanol.

The chemical structures of the compounds described in this article were established on the basis of ^{1}H and ^{13}C NMR and IR spectroscopy. All these techniques gave satisfactory results. Gel permeation chromatography (GPC) measurements (mobile phase, THF; calibration standard, polystyrene) confirmed the presence of practically monodisperse polymers in all cases. However, as often happens with dendrimers, a marked deviation from the calculated molecular weight was found in the experimental data.[20] The molecular weight of the dendrimers under study could be estimated by MALDI−TOF measurements, which confirmed the incomplete functionalization of the commercial dendrimers DAB and PAMAM with the promesogenic units in all cases (Table 1). As it can be seen, an average degree of functionalization of the dendrimers of 67% is obtained. L_6 is the promesogenic unit that is less reactive with the dendritic cores, giving rise to the lowest degrees of functionalization, probably because of rigidity imposed by the two ester linkages in its structure. Instead, the flexibility of the oxymethylene bridges present in units L_3 and L_9 favors the incorporation of a higher number of promesogenic units at the periphery of the dendrimers. We tried to confirm these data by integration of the signals obtained by ^{13}C NMR, but once again, the measurements are not accurate enough because of the difficulty of integrating the peaks corresponding to the dendrimeric core.

Mesomorphic Properties. The liquid-crystalline properties and the thermal stability of these compounds have been studied by polarizing optical microscopy, differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The thermal and thermodynamic data are gathered in Table 2.

All the dendrimers prepared show liquid-crystalline behavior. Under the optical miscroscope, a mesophase appears in all cases. The texture of the mesophase displayed by these compounds does not show any characteristic features; although, in some cases, a pseudo-focal-conic texture was identified.

Table 2. Thermal and Thermodynamic Data for the Dendrimers under Study

dendrimer	transition temperatures (°C) and enthalpies (kJ mol^{-1})[a]
DAB(L_3)32	g not observed Col$_h$ 68.5 (20.8) I
DAB(L_6)32	g 55 Col$_h$ 99.0 (8.8) I
DAB(L_9)32	g 29 Col$_h$ 112.9 (11.0) I
PAMAM(L_3)32	g 21 Col$_h$ 192.5 (5.0) I
PAMAM(L_6)32	g 33 Col$_h$ 156.7 (16.0) I
PAMAM(L_9)32	g 37 Col$_h$ 164.7 (51.5) I
DAB(L_3)64	g 42 Col$_h$ 102.3 (3.9) I
DAB(L_6)64	g 57 Col$_h$ 161.7 (42.4) I
DAB(L_9)64	g 44 Col$_h$ 166.6 (103.0) I
PAMAM(L_3)64	g 42 Col$_h$ 159.5 (17.0) I
PAMAM(L_6)32	g 55 Col$_h$ 176.0 (36.2) I
PAMAM(L_9)32	g 45 Col$_h$ 172.5 (115.1) I

[a] Data correspond to the first heating scans of the samples. Temperatures of the transitions are taken at the maximum of the peaks. Values of ΔH are shown in parentheses. g, glass; Col$_h$, hexagonal columnar mesophase; I, isotropic liquid.

Thermogravimetric analysis shows that all dendrimers remain without any loss of weight below the clearing temperature (T_i).

X-ray Diffraction Studies. Temperature-dependent X-ray diffraction experiments were carried out for the whole series of compounds in order to characterize the mesophase observed by polarizing optical microscopy and by DSC. The X-ray patterns, obtained in the temperature range given in Table 3, are qualitatively similar in all cases and are typical of the hexagonal columnar mesophase, Col$_h$. A diffuse scattering halo in the wide-angle region centered at around 4.5 Å, corresponding to the liquidlike order of the molten chains, confirmed the liquid-crystalline nature of the mesophase. Up to three and sometimes four sharp small-angle reflections, corresponding to the reciprocal spacings in the ratios 1, $\sqrt{3}$, $\sqrt{4}$, and $\sqrt{7}$, and to the indexation (hk) = (10), (11), (20), and (21), were observed in the patterns, indicative of a two-dimensional hexagonal packing of the columns. In Table 3, some of the structural parameters of the mesophase for all the dendrimers are collected.

Supramolecular Organization in the Mesophase. As it can be seen from the results gathered in Tables 2 and 3, all the compounds show a Col$_h$ phase, even in the case of the dendrimers bearing the largest mesogenic unit, L_9. The model already proposed for columnar mesophases[13,16] in high-generation dendrimers consists of a cylindrical molecular

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Table 3. X-ray Results for the Mesophases of the Dendrimers under Study[a]

compound	T (°C)	M	h	k^b	d_{obs} (Å)	a (Å)^b	s (Å^2)^b	h (Å)^c	D (Å)^c
DAB(L_3)32	40	Col$_h$	1	0	44.4	51.3	2276	18.7	53.8
			1	1	25.2				
			2	0	21.8				
					4.5^d				
DAB(L_6)32	25	Col$_h$	1	0	43.6	50.3	2195	36.6	52.9
			1	1	25.4				
DAB(L_9)32	80	Col$_h$	1	0	43.1	49.8	2145	51.0	52.3
			1	1	25.0				
DAB(L_3)64	50	Col$_h$	1	0	47.3	54.6	2583	33.1	57.3
			1	1	28.3				
			2	0	24.1				
DAB(L_6)64	25	Col$_h$	1	0	44.6	51.5	2296	70.1	54.1
			1	1	25.6				
DAB(L_9)64	80	Col$_h$	1	0	47.9	55.3	2649	82.8	58.1
			1	1	27.7				
			2	0	24.0				
					4.5^d				
PAMAM(L_3)32	60	Col$_h$	1	0	55.8	64.4	3595	13.4	67.7
			1	1	32.3				
			2	0	27.8				
			2	1	21.1				
					4.5^d				
PAMAM(L_6)32	25	Col$_h$	1	0	48.6	56.1	2727	31.6	58.9
			1	1	28.4				
PAMAM(L_9)32	50	Col$_h$	1	0	51.4	59.4	3050	37.8	62.3
			1	1	29.8				
PAMAM(L_3)64	80	Col$_h$	1	0	56.2	64.9	3647	26.7	68.1
			1	1	32.5				
			2	0	27.9				
					4.5^d				
PAMAM(L_6)64	80	Col$_h$	1	0	51.6	59.6	3074	56.2	62.6
			1	1	29.9				
					4.5^d				
PAMAM(L_9)64	80	Col$_h$	1	0	51.4	59.4	3050	75.7	62.3
			1	1	29.6				
			2	0	25.5				

[a] In each column of the table are listed, from left to right, the compound code, the temperature of the experiment, the type of mesophase, the proposed indexation, the observed spacings, and the lattice constants. [b] a: Hexagonal lattice constants from $a = (2d_{10})/\sqrt{3}$. s: Hexagonal lattice surface from $s = ad_{10}$. h, k: Miller indices. [c] h: Molecular thickness of one dendrimeric molecule along the axes of the column. D: Diameter of the column packed in the hexagonal lattice (for our calculation, we suppose that the column had a cylinder shape). [d] Broad, diffuse maximum.

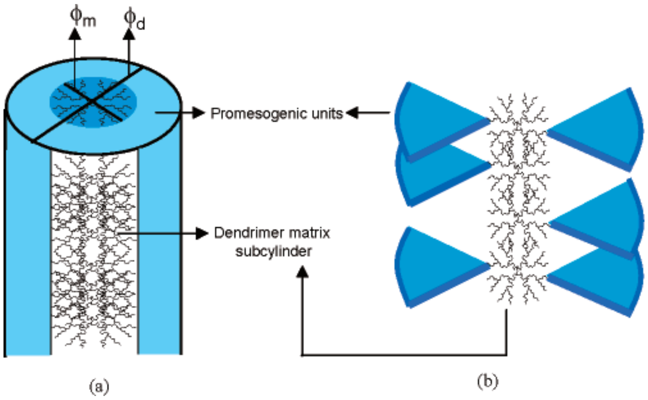

Figure 2. Schematic representation of (a) the cylindrical model for the dendrimer molecule and (b) the interaction among the promesogenic units in the cylindrical arrangement (idealized) of a partially functionalized dendrimer.

ordering, in which the dendrimer matrix (PAMAM or DAB) occupies the inner part of the cylinder and the mesogenic units are forced to spread out around the dendritic core (Figure 2a), so that the promesogenic units can interact among them in a way appropriate to maintain the cylindrical arrangement which sustains the columnar mesophase (Figure 2b).

To explain this behavior and propose a model for the molecular arrangement in the mesophase, we present here some theoretical calculations starting from the experimentally measured spacings d obtained by X-ray diffraction and the values of the molecular weight of the dendrimers assuming that the functionalization of the dendrimeric terminal amino groups is complete. Using the expressions described in the Appendix, we can estimate the values for the surface, diameter, and height of the cylinders constituted by the dendrimer as a whole, and also those of the *subcylinder* occupied by the dendritic core. The results of these calculations are collected in Table 4. Similar calculations were made for PAMAM and DAB dendrimers functionalized with 4-(4′-decyloxybenzoyloxy)-salicylaldehyde (L_1)[11] and 4-(3′,4′-didecyloxybenzoyloxy)-salicylaldehyde (L_2).[13,16] Figure 3 shows a schematic representation of the evolution of the size of the dendrimer matrix cylinder for all the considered PAMAM dendrimers [in the case of DEND(L_1), the cylinder comprises both the dendrimers matrix and the mesogenic units, since they show a lamellar mesomorphism]. As it can be seen and according to the X-ray diffraction results (Table 3), when the volume of the mesogenic units is increased, the dendrimeric core adopts a more elongated conformation, that is, the cylinder base surface decreases and the height increases, so that the peripheral units can be accommodated at the periphery, favoring, in this way, a molecular columnar arrangement. For each generation, the supermolecules with L_3 units arrange within a column whose diameter is larger than those corresponding to the dendrimers with L_6 and L_9, even though these promesogenic units are bigger than L_3. This means that the dendrimer core adopts an extended conformation which is responsible for the molecular broadening. This behavior is possible as a result of the conformational freedom of the PAMAM dendrimeric core. The lengths of the most extended conformations of PAMAM-32 (71.2 Å) and PAMAM-64 (88.1 Å), calculated by the MM2 package of CS Chem 3D Ultra 6.0, are higher than the values obtained for dendrimers containing L_9 units from our calculations. Therefore, even in a situation where complete functionalization of the dendrimer took place, a cylindrical model for the macromolecule would be feasible and would explain the occurrence of a columnar mesophase.

In the case of the DAB dendrimers, the same and even more pronounced effect is observed (Figure 3). According to our calculations, the columnar mesophase exhibited by dendrimers DAB(L_9)32, DAB(L_6)64, and DAB(L_9)64 would be explained if the macromolecules adopted a cylindrical shape with heights of 51.0, 70.0, and 82.6 Å, respectively. Obviously, this is not possible in practice because the most extended conformations of the corresponding DAB dendrimeric cores, calculated by the MM2 package of CS Chem 3D Ultra 6.0, (**DAB-32**: 44.7 Å; **DAB-64**: 54.4 Å) can never reach those values. Thus, the hexagonal columnar mesomorphism which is found for those dendrimers can only be explained by an incomplete functionalization of the terminal amino groups of DAB with mesogenic units. In this way, the calculations described above are no longer valid, since

Table 4. Values for the Surface, Diameter, and Height of the Cylinder Constituted by the Dendrimer and Subcylinder Occupied by the Dendritic Matrix from the Experimental Data *d* Obtained by XRD, Assuming a Complete Degree of Functionalization of the Dendrimers with Mesogenic Units

dendrimer	M_{wd}^{a}	V_{d}^{a}	M_{wm}^{b}	V_{m}^{b}	T (°C)	d_{exp}	S_{d}^{a}	ϕ_{d}^{a}	h_{d}^{a}	S_{m}^{b}	ϕ_{m}^{b}	h_{m}^{b}
PAMAM(L_3)32	29 086	48 291	6909	11 471	60	55.8	3595	67.7	13.4	854.0	33.0	13.4
DAB(L_3)32	25 678	42 633	3501	5813	40	44.4	2276	53.8	18.7	310.3	19.9	18.7
PAMAM(L_3)64	58 568	97 241	14215	23 601	80	56.2	3647	68.1	26.7	885.2	33.6	26.7
DAB(L_3)64	51 445	85 415	7092	11 775	50	47.3	2583	57.3	33.1	356.1	21.3	33.1
PAMAM(L_6)32	51 774	85 960	6909	11 471	25	48.6	2727	58.9	31.5	363.9	21.5	31.5
DAB(L_6)32	48 366	80 302	3501	5813	25	43.6	2195	52.9	36.6	158.9	14.2	36.6
PAMAM(L_6)64	103 945	172 580	14215	23 601	25	51.6	3074	62.6	56.1	420.4	23.1	56.1
DAB(L_6)64	96 822	160 754	7092	11 775	25	44.6	2296	54.1	70.0	168.2	14.6	70.0
PAMAM(L_9)32	69 276	115 020	6909	11 471	50	51.4	3050	62.3	37.7	304.2	19.7	37.7
DAB(L_9)32	65 868	109 361	3501	5813	80	43.1	2145	52.3	51.0	114.0	12.0	51.0
PAMAM(L_9)64	138 950	230 699	14215	23 601	80	51.4	3050	62.3	75.6	312.0	19.9	75.6
DAB(L_9)64	131 827	218 872	7092	11 775	80	47.9	2649	58.1	82.6	142.5	13.5	82.6

[a] Molecular weight and volume of the dendrimer; surface, diameter, and height corresponding to the dendrimer cylinder. [b] Molecular weight and volume of the dendritic matrix; surface, diameter, and height corresponding to the dendritic matrix subcylinder.

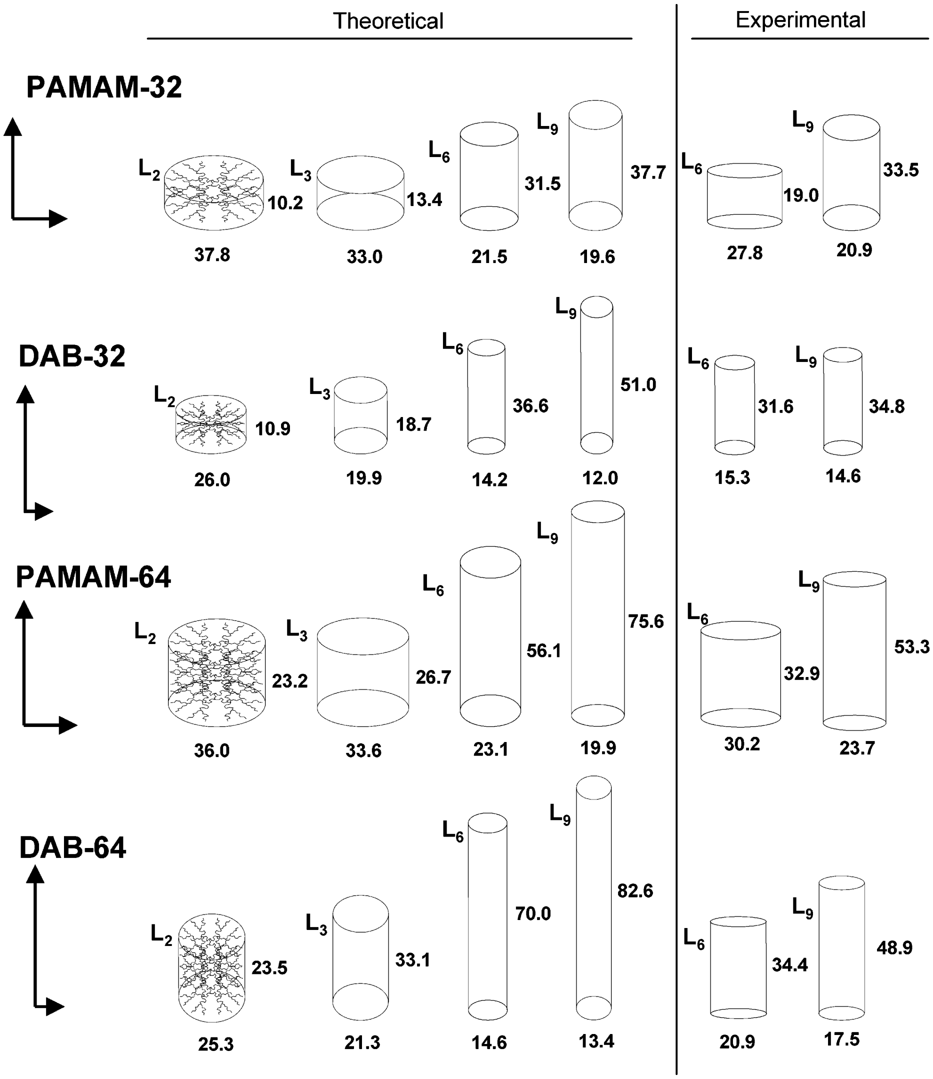

Figure 3. Theoretical and experimental values for ϕ_m and h_m (diameter and height of the subcylinder occupied by the dendrimer matrix) (Å).

the molecular weight of the final dendrimer and the proportion core/mesogenic units are not as indicated in Table 4. The number of mesogenic units that have to be accommodated around the central dendrimeric core is lower than 32 or 64 in each case, and the DAB core can adopt an extended conformation, giving rise to a cylindrical-shaped macromolecule, compatible with a columnar mesophase as the thermodynamically most stable supramolecular arrangement. In the case of complete functionalization on the periphery of the dendrimer, the compounds DAB(L_9)32, DAB(L_6)64, and DAB(L_9)64 would not present a hexagonal columnar mesophase, but they would probably adopt a globular conformation in order to accommodate the mesogenic units around the dendritic core.

As already mentioned before, GPC measurements confirmed the presence of practically monodisperse polymers in all cases, but the value obtained for the molecular weight is not reliable because a marked deviation from the real one is often found in the case of dendrimers. Mass spectrometry techniques, such as MALDI−TOF are, however, useful in this case, and the results obtained for the dendrimers are gathered in Table 1, together with the value of the degree of functionalization of the dendrimers calculated from the experimental results. The theoretical calculations gathered in Table 4 can now be remade taking into account the experimental molecular weights of the dendrimers, and the results obtained explain, in all cases, the hexagonal columnar mesophase which fits the cylindrical model proposed (Table 1 and Figure 3).

Conclusions

We have synthesized 12 mesomorphic dendrimers by functionalization of the fourth and fifth generations of amino-terminated PAMAM and DAB commercial dendrimers with bulky promesogenic units containing three, six, and nine terminal alkoxy chains. In all cases, the dendrimers exhibit a hexagonal columnar mesophase, which can be explained by a cylindrical molecular model. The driving force for this molecular symmetry which gives rise to the columnar mesophase is the strong interaction among the promesogenic units in this arrangement. According to the theoretical calculations performed from experimental XRD data, this cylindrical symmetry should not be feasible for some of the largest dendrimers, and therefore, a hexagonal columnar mesophase would not be expected. However, our experiments confirm that, even in those cases, the material exhibits such a mesomorphic behavior. This fact is explained by a partial functionalization of the dendrimers with promesogenic units.

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Appendix

Determination of the Thickness *h* of One Dendrimer along the Axis of the Column. The density ρ_{cell} of one cell can be described as

$$\rho_{\text{cell}} = \frac{M_{\text{cell}}}{V_{\text{cell}}}$$

where M_{cell} and V_{cell} are the mass and the volume of the cell, respectively.

If we assume that

$$M_{\text{cell}} = \frac{M}{N_{\text{A}}}$$

with M the molecular mass of the dendrimer and N_{A} Avogadro’s number (6.02×10^{23}), and that V_{cell} is

$$V_{\text{cell}} = s \times h \times 10^{-24} \text{ (in Å}^3\text{)}$$

we can write ρ_{cell} as

$$\rho_{\text{cell}} = \frac{\frac{M}{N_{\text{A}}}}{s \times h \times 10^{-24}}$$

If we assume that

$$\rho_{\text{cell}} = 1$$

we can deduce the expression of h as

$$h = \frac{10 \times M}{6.02 \times s}$$

Supporting Information Available: Experimental section containing techniques, the synthesis, and the analytical data of the dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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