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Molecular morphology and mesomorphism in dendrimers: a competition between rods and discs†

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The synthesis and liquid crystalline behaviour of several sixteen-branched dendrimers based on poly(amidoamine) (PAMAM) and poly(propyleneimine) (DAB) are reported. Mono-, di- and trialkoxybenzoyloxysalicylaldehydes are used as mesogenic promotor moieties and are attached at the peripheral amino groups of the pre-existing dendrimers. All the compounds exhibit liquid crystalline properties which were studied by optical microscopy, DSC and X-ray diffraction. The relationship between the structure of the mesogenic units and the mesomorphic behaviour is discussed and models for the different supramolecular organizations are proposed.

Introduction

Dendrimers as materials comprised of molecules of well-defined structure offer interesting opportunities in materials chemistry.[1] In this sense, the use of dendrimers as building blocks for the construction of supramolecular architectures has attracted the interest of many research groups. As a result of new investigations, a large amount of materials have been reported in which the dendritic topology is combined with the presence of different functionalities within the macromolecular structure.[2] The interest of these materials lies in their molecular properties that arise from the multiplicative effect of the functionalities due to the dendritic structure.

When dealing with self-organizing materials, correlations between molecular morphology and macroscopic symmetry become important both from a fundamental and from a practical point of view.[3] The conformation of branched dendrimers evolves from an open, extended form to a globular shape as the generation number increases,[4] until a critical branched state, the so-called "starburst dense packing", is reached and prevents any further growth of the dendrimer.[5] X-Ray and small angle neutron scattering experiments have shown that the higher generations of PAMAM (poly(amidoamine)) and DAB (poly(propyleneimine)) dendrimers have a spherical shape.[6] However, the introduction of certain groups covalently bonded to the dendrimeric skeleton in the aim of obtaining functionalized materials (such as mesogenic units to obtain liquid crystal dendrimers) leads to the modification of the molecular conformation and therefore to a completely different macroscopic symmetry.

Dendrimeric liquid crystals can be considered as the third group of liquid crystalline, high molecular weight compounds, besides the main-chain and side-chain liquid crystal polymers. In general, dendrimers with liquid crystalline properties can be achieved with a shape-persistent, disc-like skeleton,[7] by using mesogenic flexible units as branch junctures[8] or by functionalising the dendrimer periphery with mesogenic units.[9]

Our previous work on liquid crystalline dendrimers used the latter strategy.[10–12] We have functionalized the commercially available dendrimers PAMAM and DAB with different mesogenic units and studied the influence of this structural variation on the mesomorphic behaviour of the dendrimers. We found that the modification of the PAMAM dendrimer with mesogenic units at the periphery gives rise to a material which exhibits a smectic A (SmA) mesophase. This type of supramolecular organization is not compatible with a globular molecular shape. Therefore, two driving forces compete in this case: the central PAMAM starburst polymer leads to a spherical disordered arrangement (entropic contribution), while the mesogenic terminal units tend to interact with each other to form parallel aggregations that give rise to the liquid crystal state (enthalpic contribution). The investigation of the supramolecular liquid crystal organization allowed us to propose a model for the dendritic macromolecules and for the molecular arrangement in the mesophase.[10] This model is in accordance with the results reported by other authors concerned with the study of different mesomorphic dendritic systems.[9d,g,h] Therefore, these liquid crystal dendrimers can be considered as block molecules, in analogy to high molecular weight block copolymers, since they are made up of at least two incompatible parts, the dendritic core and the terminal groups, and this tends to afford a microphase-separated structure.[13] 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 on the structure of the mesomorphic unit.

The structural modification of the mesogenic units attached to the dendritic skeleton, such as the grafting of additional terminal aliphatic chains, leads to mesomorphic materials which exhibit columnar mesomorphism. In this case, a model has been proposed on the basis of experimental results.[12]

As far as dendritic balls are concerned, we have recently reported on the results obtained for materials comprised of amphiphilic molecules resulting from the marriage between a classical thermotropic discotic molecule and carbohydrate-based amphiphilic dendrons.[14] These compounds behave as amphiphilic materials with two well-defined molecular regions – the central hydrophobic part and the peripheral hydrophilic one. As a consequence of this microsegregation, they exhibit

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amphotropic liquid crystalline behaviour, *i.e.* both thermotropic and lyotropic mesomorphism. The balance between the two different molecular regions controls the existence of mesomorphism and the type of columnar arrangement observed in the mesophase.

In this paper, we describe the synthesis, and the chemical, thermal and structural characterization of two families of liquid crystalline dendrimers, in which the relationship between molecular structure and mesomorphic behaviour is clearly established. The dendrimers (Fig. 1) are based on the dendrimer PAMAM (third generation) (PAMAM[L(14)$_n$]$_{16}$) and DAB (third generation) (DAB[L(14)$_n$]$_{16}$), functionalized with sixteen mesogenic units, in which the terminal benzene ring is mono- ($n=1$), di- ($n=2$) or trisubstituted ($n=3$) with tetradecyloxy chains.

In order to introduce an additional comparative element in this structure–mesomorphic behaviour relationship study, a DAB-derived dendrimer containing sixteen laterally grafted mesogenic units[15] (D_{16}), which exhibits a nematic mesophase, is also included (Fig. 2).

Experimental

Methods and materials

The dendrimers were synthesized by the condensation of the appropriate salicylaldehyde with the terminal amino groups of the third generation of dendrimer PAMAM and of the third generation of dendrimer DAB. All the compounds were isolated as air-stable solids that are soluble in solvents such as dichloromethane, chloroform and THF and insoluble in ethanol. The chemical structures of the dendrimers were established on the basis of ^{1}H and ^{13}C NMR and IR spectroscopy, gel permeation chromatography (GPC) and elemental analysis. All these techniques afforded satisfactory results. IR, ^{1}H and ^{13}C NMR spectroscopy have proven to be very useful in confirming the structure and the purity of these materials. Evidence for the condensation reactions was provided by the absence of a signal at $\delta=195$ ppm in the ^{13}C NMR spectra (the carbonyl group of the aldehyde) along with the complete absence of the signals corresponding to the amino group from the starting material both in the ^{1}H NMR and IR spectra. GPC measurements confirmed in all cases the presence of practically monodisperse polymers.

Microanalyses were performed with a Perkin Elmer 240B microanalyzer. Infrared spectra were obtained with a Perkin Elmer 1600 (FTIR) spectrophotometer in the 400–4000 cm^{-1} spectral range. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in $CDCl_3$ solutions. Gel permeation chromatography (GPC) was carried out in a Waters liquid chromatography system equipped with a 600E multi-solvent delivery system and 996 photodiode array detector. Two Ultrastyragel columns (Waters, pore size 500–10^4 Å) were connected in series. THF was used as the mobile phase with a flow rate of 0.8 mL min^{-1}. Calibration was performed with polystyrene standards.

The optical textures of the mesophases were studied with a Nikon polarizing microscope equipped with a Mettler FP8 hot stage and a FP80 central processor. The transition temperatures and enthalpies were determined by differential scanning calorimetry with a Perkin Elmer DSC-7 instrument operated at a scanning rate of 10 min^{-1} on heating. The apparatus was calibrated with indium (156.6 °C, 28.4 J g^{-1}) as a standard. The XRD patterns were obtained with two different experimental set-ups, and in all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter. i) The characterization of the wide-angle region and the measurements of the periodicities were achieved using a linear monochromatic Cu-Kα_1 beam obtained with a sealed-tube generator (900 W) and a bent quartz monochromator was used. One set of diffraction patterns was registered with a curved counter Inel CPS 120, for which the sample temperature was controlled within ±0.05 °C. ii) XRD patterns were also obtained using a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-Kα beam. The sample was heated, when necessary, with a variable-temperature attachment. The diffraction pattern was collected on flat photographic film.

General procedure for the preparation of the dendrimers

To a stirred solution of the appropriate salicylaldehyde (1.6 mmol) in CH_2Cl_2 (25 mL) was added neutral activated grade 1 alumina (0.8 g) and then the poly(amidoamine) or poly(propyleneimine) dendrimer (0.1 mmol). The mixture was refluxed under nitrogen until the aldehyde had completely reacted (usually 8–10 h). The alumina was filtered off and the solvent removed under vacuum. The product was purified by column chromatography (CH_2Cl_2–hexane 1 : 2). Yield: 60–75%.

Characterization

^{1}H and ^{13}C NMR spectra of PAMAM[L(14)$_2$]$_{16}$ and DAB-[L(14)$_3$]$_{16}$ are given as representative examples. The characterization data obtained by other techniques are quoted for all the dendrimers.

PAMAM[L(14)$_1$]$_{16}$. IR (Nujol): ν/cm^{-1} = 3339, 3280 (CON–H), 1727 (OC=O), 1655 (sh OC–NH), 1635 (CH=N); elemental analysis calcd for $C_{590}H_{864}N_{58}O_{92}$ (%): C 69.19, H 8.50, N 7.93; found C 69.2, H 8.3, N 7.8.

PAMAM[L(14)$_2$]$_{16}$. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=13.9$ (s, 1H), 8.22 (s, 1H), 7.71 (d, $J=9$ Hz, 1H), 7.55 (s, 1H), 7.14 (d, $J=9$ Hz, 1H), 6.85 (d, $J=9$ Hz, 1H), 6.66 (s, 1H), 6.56 (d, $J=9$ Hz, 1H), 4.0 (s, 4H), 3.65 (s, 2H), 3.45 (s, 2H), 3.19 (s, 2H), 2.66 (s, 2H), 2.49 (s, 2H), 2.20 (s, 4H), 1.81 (m, 4H), 1.38 (m, 2H), 1.3 (s, 36H), 0.82 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=173.12$, 172.60, 165.80, 164.63, 164.18, 154.64, 153.97, 148.66, 134.91, 132.79, 132.04, 130.30, 126.49, 124.50, 124.04, 121.11, 116.22, 116.06, 114.50, 114.18, 112.11, 111.86, 110.76, 77.22, 69.34, 69.03, 57.27, 53.42, 52.32, 50.12, 39.99, 37.33, 36.19, 34.02, 31.92, 31.71, 29.72, 29.66, 29.45, 29.37, 29.23, 29.08, 26.06, 26.0, 25.22, 22.68, 14.33; IR (Nujol): ν/cm^{-1} = 3294, 3268 (CON–H), 1725 (OC=O), 1655 (sh OC–NH), 1633 (CH=N); elemental analysis calcd for $C_{814}H_{1312}N_{58}O_{108}$ (%): C 71.68, H 9.69, N 5.95; found C 71.6, H 9.7, N 6.0.

PAMAM[L(14)$_3$]$_{16}$. IR (Nujol): ν/cm^{-1} = 3290, 3075 (CON–H), 1731 (OC=O), 1656 (sh, OC–NH), 1641.6 (CH=N); elemental analysis calcd for $C_{1038}H_{1760}N_{58}O_{124}$(%): C 73.17, H 10.41, N 4.77; found: C 73.3, H 10.2, N 4.8.

DAB[L(14)$_1$]$_{16}$. IR (Nujol): ν/cm^{-1} = 1728 (OC=O), 1632 (CH=N); elemental analysis calcd for $C_{536}H_{784}N_{30}O_{64}$ (%): C 74.33, H 9.11, N 4.84; found: C 74.4, H 8.9, N 4.9.

DAB[L(14)$_2$]$_{16}$. IR (Nujol): ν/cm^{-1} = 1725 (OC=O), 1633 (CH=N); elemental analysis calcd for $C_{760}H_{1232}N_{30}O_{80}$ (%): C 75.63, H 10.29, N 3.48; found: C 75.8, H 10.0, N 3.4.

DAB[L(14)$_3$]$_{16}$. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=14.0$ (s, 1H), 8.23 (s, 1H), 7.32 (s, 2H), 7.15 (s, 1H), 6.70 (d, $J=9$ Hz, 1H), 6.59 (d, $J=9$ Hz, 1H), 3.97 (s, 6H), 3.88 (s, 2H), 2.43 (s, 4H), 1.74 (s, 4H), 1.43 (s, 6H), 1.22 (s, 66H), 0.84 (t, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=164.47$, 164.29, 163.51, 154.22, 152.95, 143.11, 132.25, 123.62, 116.4, 112.05, 110.71, 108.55, 105.74, 78.30, 77.97, 77.42, 73.54, 73.39, 69.24, 56.0, 55.55, 52.84, 52.54, 52.23, 52.04, 51.53, 51.05, 31.91, 31.39, 31.05, 30.94, 30.65, 30.38, 29.74, 29.70, 29.66, 29.43, 29.36, 28.71,

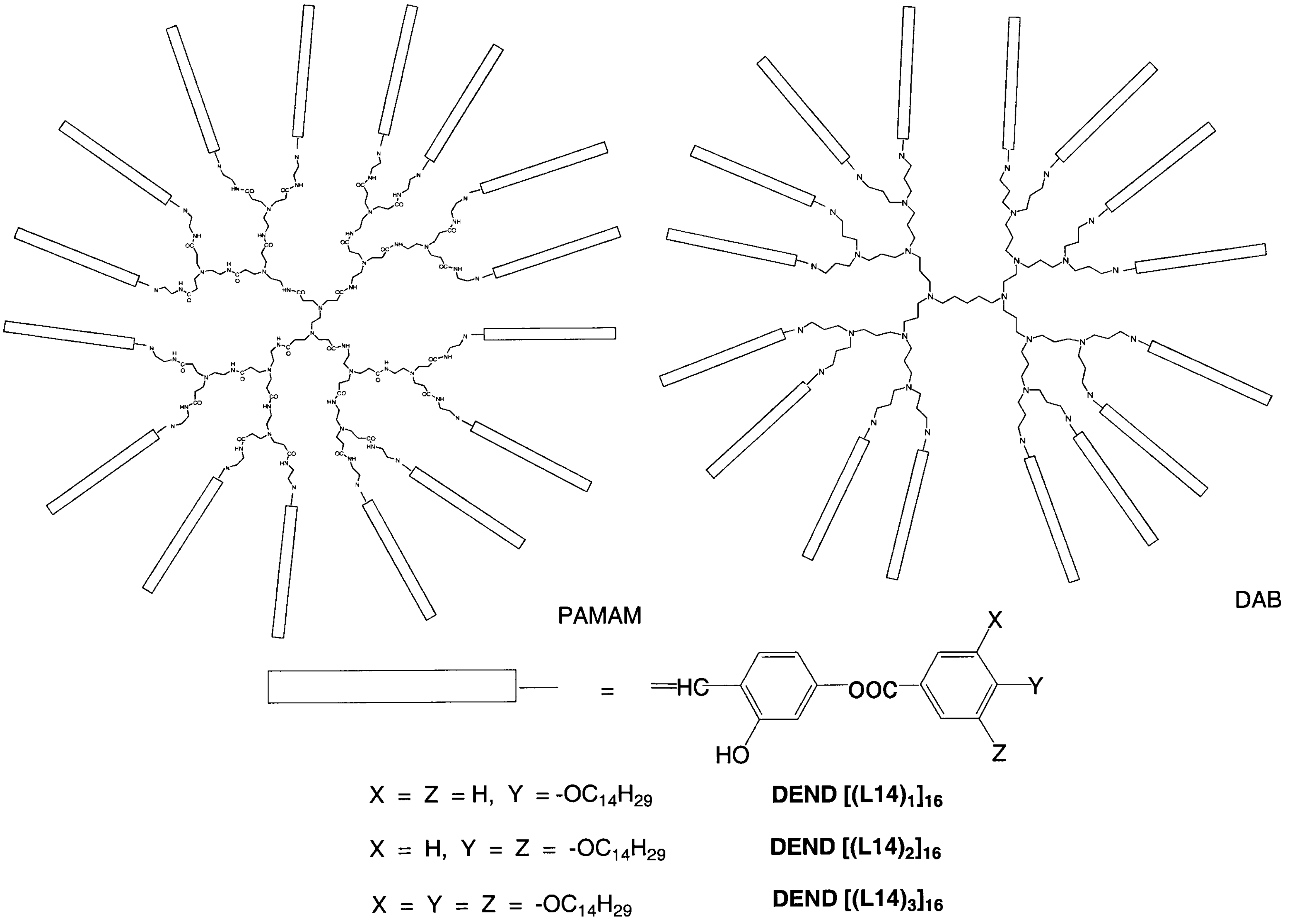
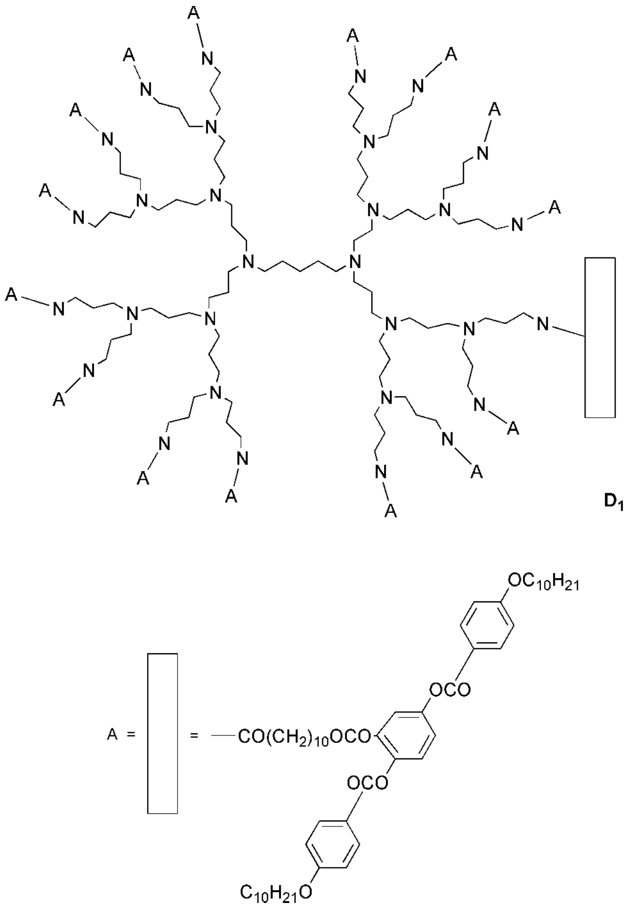


Fig. 1 Chemical structures and nomenclature of the dendrimers.



D16

Fig. 2 Chemical structure of dendrimer D_{16}.

28.47, 27.87, 27.16, 26.13, 24.24, 23.76, 22.89, 22.67, 14.08; IR (Nujol): ν/cm^{-1} = 1736 (OC=O), 1631 (CH=N); elemental analysis calcd for $C_{984}H_{1680}N_{30}O_{96}$ (%): C 76.41, H 10.95, N 2.72; found: C 76.5, H 10.8, N 2.8.

Results and discussion

Mesomorphic properties

The behaviour of the dendrimers as liquid crystal materials was investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC) prior to X-ray diffraction (XRD) experiments. Thermal and thermodynamic data for the seven dendrimers are gathered in Table 1.

These dendrimers behave as typical polymers and, in general, the DSC thermograms in the first heating scan show broad peaks corresponding to the phase transitions. However, in the cooling and in the second heating scans, more simple thermograms are obtained, and they are reproducible in subsequent scans. The DSC curves of all the compounds are qualitatively similar and present two or three endotherms which indicate the appearance of three or four different phases. In most cases, an anisotropic glass-to-mesophase as well as a mesophase-to-isotropic liquid transition can be observed.

Table 1 Transition temperatures[a]/°C and transition enthalpies (kJ mol^{-1}; in parentheses) of the PAMAM- and DAB-derived dendrimers

Dendrimer	Phase transition
PAMAM[L(14)$_1$]$_{16}$	g 27.7 SmA 191.6 I + dec.
PAMAM[L(14)$_2$]$_{16}$	g 46.6 Col$_H$ 200.5 (18.9) I
PAMAM[L(14)$_3$]$_{16}$	K 28.0 (694.8) Col$_H$ 55.0[b] I
DAB[L(14)$_1$]$_{16}$	g 18.9 SmA 121.8 (18.2) I
DAB[L(14)$_2$]$_{16}$	K 39.4 (261.9) Col$_H$ 105.0 (65.4) I
DAB [L(14)$_3$]$_{16}$	g 10.8 Col$_H$ 44.7 (61.1)
D$_{16}$	g 17.6 SmC[c] 38.5 (34.0) N 65.1 (26.3) I

[a]The thermal data given correspond to the second heating DSC scan. The transition temperatures reported are the DSC peak maximum values. [b]Transition detected by optical microscopy. [c]Modulated mesophase.

The mesomorphic character of these dendrimers was firstly detected by observing the optical textures of the mesophases under a polarized-light microscope. This technique is not totally reliable in order to obtain unequivocal information for the assignment of the type of mesophase. Nevertheless, some specific textures associated with the nematic and smectic A mesophases could be easily recognized. The columnar mesophases do not show any characteristic feature although in some cases a broken fan-like texture can be identified. An overall view of the results reveals that dendrimers with one terminal chain in the mesogenic units (DEND[L(14)$_1$]$_{16}$ afford a lamellar mesophase (SmA type). When the mesogenic units are laterally grafted to the dendrimeric scaffold (compound D$_{16}$), the dendrimer shows a nematic mesophase and an ordered phase at lower temperatures. This result resembles the behaviour of nematic side chain polymers including laterally attached mesogenic units.[16] In these polymers the parallel alignment of mesogens is hindered and prevents the formation of a positionally ordered mesophase, but still allows a preferred orientational ordering of mesogenic units that gives rise to the nematic phase. However, dendrimers incorporating mesogenic units with two terminal chains present a columnar phase, with a broader temperature range for the PAMAM than for the DAB derivatives. When three terminal chains are attached onto the peripheral mesogenic units, the dendrimers also present a columnar mesophase. In this case, a drastic decrease of the clearing temperature (T_i, mesophase-to-isotropic liquid transition temperature) is observed for both PAMAM and DAB dendrimers. Therefore, passing from two to three terminal chains in the mesogenic units leads to a decrease of the domain stability of the columnar mesophase.

It is also noteworthy that PAMAM dendrimers present more stable mesophases than the DAB derivatives: higher T_i values but similar T_g's. This fact can be explained taking into account the existence of intra- and intermolecular H-bonds in the poly(aminoamine) dendrimer which do not occur in the case of the poly(propyleneimine) one. These H-bonds undoubtedly contribute to certain rigidification of the central branching core and therefore enhance the cohesion of the supramolecular organizations, *i.e.* lamellae or columns.

X-Ray diffraction studies

All the compounds were studied by X-ray diffraction in their mesophases. The results obtained confirm in all cases the microscopic observations, and make it possible to unequivocally assign the type of mesophase as well as to determine the parameters of the supramolecular structures. The measured periodicities are gathered in Table 2.

As shown, the spacing of the SmA phase decreases quite substantially when the temperature increases. This fact can be explained in terms of the higher conformational freedom of both the terminal hydrocarbon chains and the central branched moiety, as well as the orientational fluctuations of the rigid mesogenic units. This phenomenon, which is already known in classical mesogens, is magnified by the high number of flexible units in this particular type of liquid crystal that contain a large central dendritic scaffold.

For dendrimers with both two and three terminal alkoxy chains a hexagonal columnar mesophase is formed. The periodicities d_{10} given in Table 2, are dependent on the thermal treatment applied to the sample under study: the values measured in samples cooled from the isotropic liquid phase are smaller than those obtained for virgin samples. This might

Table 2 X-Ray diffraction data for the SmA and the $\mathrm{Col_h}$ mesophases of the dendrimers: temperature of the experiment and measured spacing d_{001} or d_{10}[a]

Compound	T/°C	Mesophase	d_{001}/Å	d_{10}/Å
$\mathrm{PAMAM[L(14)_1]_{16}}$	90	SmA	64	
	135	SmA	55	
$\mathrm{DAB[L(14)_1]_{16}}$	22	SmA	60	
	110	SmA	51	
$\mathrm{PAMAM[L(14)_2]_{16}}$	100	$\mathrm{Col_h}$		60
$\mathrm{DAB[L(14)_2]_{16}}$	80	$\mathrm{Col_h}$		55
$\mathrm{PAMAM[L(14)_3]_{16}}$	22[b]	$\mathrm{Col_h}$		55
$\mathrm{DAB[L(14)_3]_{16}}$	22	$\mathrm{Col_h}$		54.5
	22[b]	$\mathrm{Col_h}$		51.5

[a] d_{001} is the layer spacing that is directly measured from the patterns. d_{10} is the measured spacing for the (10) reflection of the 2D hexagonal lattice. The lattice constant is deduced as $\boldsymbol{a}_{\mathrm{hex}}=2d_{10}/\sqrt{3}$. Higher order reflections were obtained with the spacing ratio $\sqrt{1}$, $\sqrt{3}$ and $\sqrt{4}$, which prove the hexagonal 2D symmetry. [b] After heating the sample to the isotropic liquid and cooling to room temperature.

well be due to the conformational disorder of the flexible units when submitted to a thermal treatment which persists when cooled again and produces a decrease in the effective molecular diameter. In general, the spacings determined for the DAB-derived dendrimers are smaller than those corresponding to their PAMAM-derived homologues, and this is a consequence of the substantial differences of the molecular volumes of both dendritic cores.

Supramolecular organization in the mesophase

As shown in Table 1, dendrimers which incorporate just one tetradecyloxy terminal chain in the mesogenic units show a lamellar SmA mesophase according to the previously proposed cylindrical model[10] (Fig. 3), whereas the presence of two and three terminal chains prevents the formation of a lamellar structure and instead, a columnar arrangement is favoured. The structural change due to the introduction of one or two additional alkoxy chains in the mesogenic unit modifies the relationship between the hard part (mesogenic units) and the soft part of the dendrimer (PAMAM and DAB central structures and alkoxy terminal chains). As a consequence, the molecular interactions are also modified and the formation of a lamellar structure is hindered since a higher number of aliphatic chains requires a larger volume, in such a way that they cannot be accommodated in a cylindrical morphology, but forced to spread out *around* the central dendritic core. This gives rise to a molecular disc-like conformation. A similar behaviour has already been observed for certain low molecular weight mesogens.[17]

The columnar mesophase results from the stacking of the molecules in this conformation as sketched in Fig. 3. The driving force which governs this type of supramolecular columnar organization is the microphase separation between the incompatible segments of the macromolecule, namely the curly arrangement of the flexible dendrimer, the concentric rigid aromatic belt and the peripheral soft crown.[13] It is interesting to remark that the presence of sixteen additional terminal chains (in the case of trisubstituted mesogenic units) still allows a columnar structure to occur, indicating that the mesomorphic dendrimer does not adopt in this case, a globular shape as a consequence of an increase of the molecular volume.

Finally, the introduction of laterally attached mesogenic units ($\mathrm{D_{16}}$) makes the side-by-side molecular order characteristic of the lamellar phases difficult, and favours the nematic order.

Conclusions

The mesomorphic properties of seven dendrimer liquid crystalline materials have been studied. All the dendrimers contain sixteen mesogenic units in their structures. The interactions between mesogenic units and the microphase separation of the flexible dendritic and rigid mesogenic moieties govern the type of supramolecular organization which is developed giving rise to nematic, smectic and columnar mesophases. Such a molecular design favours the enthalpic contribution, which is the predominant effect when the mesogenic units are organized in a lamellar system or in columnar mesophases.

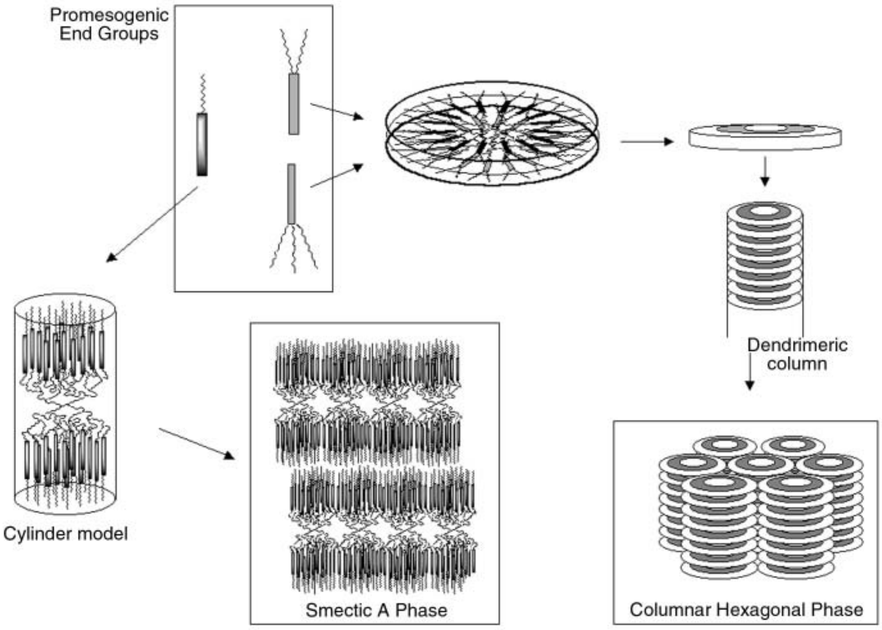


Fig. 3 Schematic representation of the molecular shapes of the dendrimers and models proposed for the supramolecular organizations (smectic A and columnar hexagonal).

Acknowledgements

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