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Dendrimers with laterally grafted mesogens

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Nematic liquid crystalline phases have been obtained by attaching mesogenic units in a lateral manner to the periphery of dendrimer generations 1, 2, 3, 4 and 5 of poly(propyleneimine). Powder XRD studies of the compounds have been performed in order to confirm the natures of the mesophases. Patterns obtained from oriented samples show a nematic phase in which the molecules are preferentially aligned in the stretching direction and also indicate the presence of local smectic C fluctuations. All compounds display an additional low temperature mesophase. Careful study of the XRD patterns of these low temperature phases has led to their assignment as a modulated Sm$\tilde{C}$ mesophase.

1. Introduction

Dendrimeric materials have recently become of great interest in supramolecular chemistry, mainly due to the possibility of obtaining well defined macromolecules [1]. Many researchers are taking advantage of commercially available dendrimers with reactive terminal groups to which new moieties with specific functions can be attached. For example, liquid crystalline dendrimers can be obtained by grafting mesogenic or promesogenic units in the peripheral positions. In this respect, results reported by Shibaev [2], Frey [3], Lattermann [4], Meijer [5], Goodby [6], Hult [7], Tschierske [8], and Yonetake [9] (and their co-workers) are remarkable. Apart from this approach, many different dendritic structures have been found to be compatible with the formation of liquid crystals [10].

One of our areas of interest concerns the way in which the structure of the peripheral units modifies the liquid crystalline properties of the dendrimer [11]. In this context, we have previously reported the synthesis and characterization of polyamidoamine (PAMAM) dendrimers in which the mesomorphism can be tuned to give lamellar or columnar arrangements depending on the structure of the peripherally attached promesogenic units [11 *a*, *b*]. More specifically, mesomorphic compounds are formed when a promesogenic unit like 4-(4-decyloxybenzoyloxy)-2-hydroxybenzaldehyde is attached to the terminal amine groups of the dendrimers poly(amidoamine) (PAMAM) [11 *a*] or poly(propyleneimine) (DAB) [11 *c*]. Most of the resulting dendrimers (with one exception) exhibit smectic mesophases (SmA in the PAMAM derivatives and SmA and SmC in the DAB series).

The viscosity of these lamellar dendrimers is usually high, which would make the applicability of these materials very limited. One way to overcome this problem would be the use of less viscous mesomorphic dendrimers, which could be obtained if they displayed nematic phases [6 *g*, 12]. Nematic phases are the least viscous LC phases and have been used extensively in a range of applications. With this aim in mind we envisaged the use of an approach similar to that employed in side group liquid crystalline polymers [13, 14]. In these systems, it has been demonstrated that the introduction of laterally attached mesogenic units makes it difficult for the units to adopt the side by side molecular arrangement typical of lamellar phases, thus favouring nematic ordering [6 *g*, 6 *h*].

In this paper we present the synthesis and properties of new dendritic liquid crystalline materials in which the mesogenic units are laterally attached to a dendrimeric core derived from poly(propyleneimine) [DAB-$(NH_2)_n$]. The series consists of five new compounds $\mathbf{D}^n$ ($n = 4$, 8, 16, 32, 64) that contain 4, 8, 16, 32 and 64 peripheral laterally grafted mesogenic units attached to generations 1, 2, 3, 4 and 5, respectively, of the poly(propyleneimine) dendrimer.

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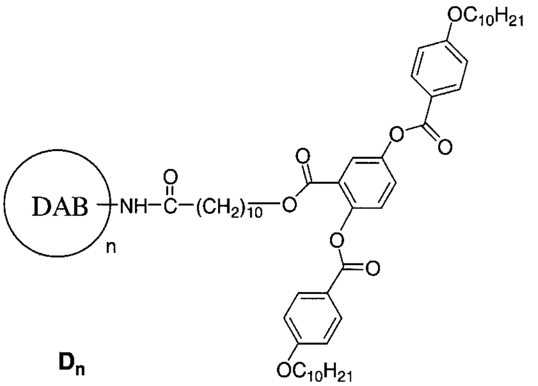


Different generations (G) of poly(propyleneimine) dendrimer
n = 4 G1 (compound $\mathbf{D_4}$)
n = 8 G2 (compound $\mathbf{D_8}$)
n =16 G3 (compound $\mathbf{D_{16}}$)
n =32 G4 (compound $\mathbf{D_{32}}$)
n =64 G5 (compound $\mathbf{D_{64}}$)

Figure 1. Structure of the dendrimers studied in this work.

2. Experimental

2.1. *Synthesis*

The dendrimers were prepared by following the synthetic pathway shown in the scheme below.

The synthesis of compound **2** was carried out through a solid–liquid phase transfer reaction between the potassium salt of 2,5-dihydroxybenzoic acid and the bromo derivative **1**, catalysed by tetrabutylammonium bromide (TBAB) following the method described by Keller [14]. Compound **3** was prepared by esterification of 4-decyloxybenzoic acid with **2**, using dicyclohexylcarbodiimide (DCC) and 4-*N*,*N*-dimethylaminopyridine (DMAP) as catalyst [15]. Deprotection of **3** with palladium hydroxide on carbon and cyclohexene yielded **4**, and subsequent formation of the pentafluorophenyl ester using DCC yielded **5**. Finally, **5** was coupled to different generations of poly(propyleneimine) [DAB-$(NH_2)_n$] to give dendrimers $\mathbf{D}^n$ ($n = 4$, 8, 16, 32, 64), where *n* equals the number of functional groups, by following a method similar to that described by Meijer *et al.* [5]. This coupling was performed by reacting the amine-functionalized dendrimer with a small excess of the pentafluoro derivative **5**.

In a general procedure for the preparation of the liquid crystalline dendrimers, a solution of DAB$(NH_2)_n$ ($n = 4$, 8, 16, 32, 64, 1 eq) in dichloromethane (2 ml) was added slowly to a solution of the activated ester (1 g, *n* eq) in dichloromethane (40 ml). The solution was stirred for 4 days, diluted with dichloromethane (50 ml) and methanol (10 ml), and shaken with saturated sodium carbonate solution. The aqueous phase was again washed with dichloromethane and the combined organic phases were dried over anhydrous sodium sulphate and concentrated *in vacuo*. The crude product was purified by column chromatography using dichloromethane/hexane (1/2) as eluent; yield 35–40%.

2.2. *Characterization*

Elemental analyses were performed with a Perkin-Elmer 240B microanalyser. Infrared spectra were obtained with a Perkin-Elmer 1600 (FTIR) spectrophotometer in the range $\nu = 400$–$4000\,\mathrm{cm^{-1}}$; ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in $CDCl_3$ solutions. Mass spectra were obtained with a VG Autospec spectrometer with LSIMS (FAB$^+$). The optical textures of the mesophases were studied with a Nikon polarizing microscope equipped with a Mettler FP8 hot stage and an FP80 central processor. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 operated at a scanning rate of 10°C $\mathrm{min^{-1}}$ on heating. The apparatus was calibrated with indium (156.6°C; 28.4 J $\mathrm{g^{-1}}$) as the standard. The XRD patterns were obtained using a pinhole camera (Anton–Paar) operating with a point-focused Ni-filtered Cu-K_α beam. The samples were held in Lindemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable-temperature attachment. The diffraction patterns were collected on flat photographic film.

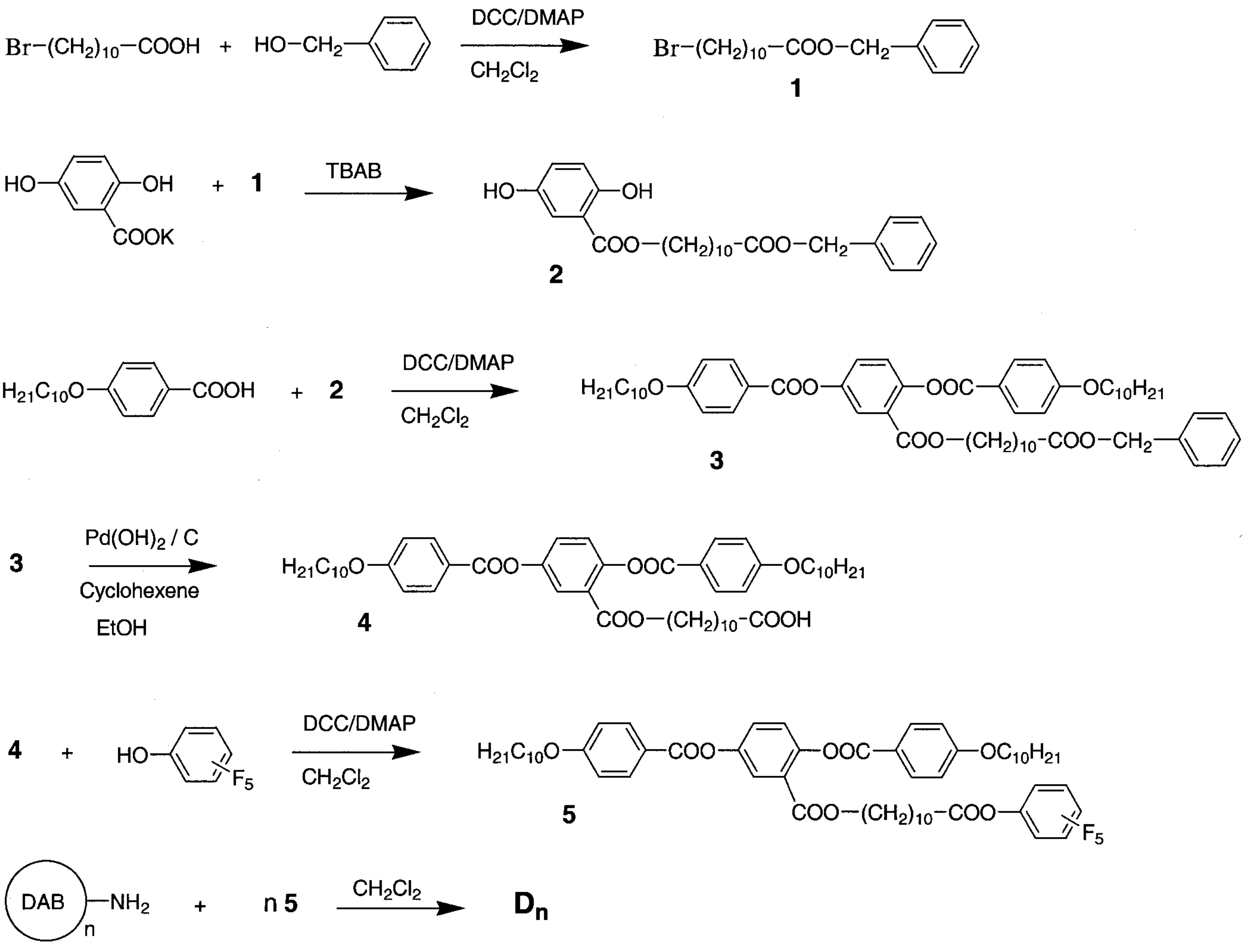
The purity of each compound (intermediates and dendrimeric compounds) was confirmed by elemental analysis, NMR (^{1}H and ^{13}C) and IR spectroscopy, and mass spectrometry (only for $\mathbf{D_4}$—the molecular masses of the higher generations could not be measured by this technique). The data are in full agreement with the structures proposed.

Due to the similarity of the NMR spectra (^{1}H and ^{13}C) of these materials, only the NMR data for the $\mathbf{D_{16}}$ dendrimers are given as a representative example.

$\mathbf{D_4}$: IR (Nujol, $\mathrm{cm^{-1}}$) ν 3311 (CON–H), 1730 (OC=O), 1712 (OC=O), 1641 (OC–NH). Anal: calcd for $C_{224}H_{328}N_6O_{36}$, C 73.09, H 8.98, N 2.28; found, C 72.9, H 9.0, N 2.3%. FAB$^+$-MS (3-NBA matrix): 3712 $[M + Na]^+$.

$\mathbf{D_8}$: IR (Nujol, $\mathrm{cm^{-1}}$) ν 3304 (CON–H), 1726 (OC=O), 1709 (OC=O), 1640 (OC–NH). Anal: calcd for $C_{456}H_{672}N_{14}O_{72}$, C 73.00, H 9.03, N 2.61; found, C 72.8, H 9.1, N 2.8%.

$\mathbf{D_{16}}$: IR (Nujol, $\mathrm{cm^{-1}}$) ν 3291 (CON–H), 1728 (OC=O), 1640 (OC–NH). Anal: calcd for $C_{920}H_{1360}N_{30}O_{144}$, C 72.96, H 9.05, N 2.77; found, C 72.8, H 9.1, N 2.7%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, $J = 9$ Hz, 2H), 8.09 (d, $J = 9$ Hz, 2H), 7.85 (d, $J = 3$ Hz, 1H), 7.40 (dd, $J = 9$ Hz, $J = 3$ Hz, 1H), 7.22 (d, $J = 9$ Hz, 1H), 7.19



Scheme.

(br s, 1H), 6.94 (d, $J = 9$ Hz, 4H), 4.09 (t, 2H), 4.00 (t, 4H), 3.19 (br s, 2H), 2.40 (br s, 2H), 2.34 (s, 2H), 2.11 (s, 2H), 1.77 (t, 4H), 1.69–1.00 (m, 44H), 0.86 (t, 6H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 173.7, 164.9, 164.5, 164.0, 163.7, 163.6, 148.3, 148.1, 132.4, 132.3, 127.1, 125.0, 124.9, 121.4, 120.9, 114.4, 114.3, 68.3, 65.6, 51.8, 51.2, 37.6, 36.6, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.4, 26.9, 26.0, 25.8, 22.7, 14.1.

$\mathbf{D}_{32}$: IR (Nujol, cm^{-1}) ν 3303 (CON–H), 1727 (OC=O), 1639 (OC–NH). Anal: calcd for $C_{1848}H_{2736}N_{62}O_{288}$, C 72.94, H 9.06, N 2.85; found, C 72.9, H 9.1, N 2.8%.

$\mathbf{D}_{64}$: IR (Nujol, cm^{-1}) ν 3335 (CON–H), 1726 (OC=O), 1644 (OC–NH). Anal: calcd for $C_{3704}H_{5488}N_{126}O_{576}$, C 72.93, H 9.07, N 2.89; found, C 72.8, H 9.1, N 2.8%.

3. Results and discussion

3.1. *Mesomorphic properties*

The mesomorphic properties of the functionalized dendrimers were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). Optical, thermal and thermodynamic data for the second heating and cooling processes of the dendrimers are gathered in table 1. In the first heating cycle all of the dendrimers showed a broad crystal to isotropic liquid transition (figure 2). On the first cooling cycle all of the dendrimers showed a nematic mesophase, which was identified in each case by the schlieren texture observed by POM. No changes in the texture were observed upon cooling the nematic mesophase further, although these dendrimers did exhibit a DSC peak at lower temperatures. This fact indicates the existence of another phase transition, which was assigned by XRD studies as a transition to a low temperature mesophase, *vide infra*. In the case of compound $\mathbf{D}_{64}$ the low temperature mesophase was only detected by XRD. The second cooling cycles were identical to the first in each case. The results for the second heating cycles were found to depend on the ease of crystallization of the

Table 1. Thermal and thermodynamic data for the phase transitions of the dendrimers.

LC dendrimer	DSC cycle	T/°C (ΔH/kJ mol^{-1})	$\Delta H_{\text{I-N}}$/m.u.[a]
$\mathbf{D_4}$	2nd heating cooling	g 23 Cr 91.6 (131.2) I I 67.5 (5.6) N 38.3 (19.5) Sm$\tilde{C}$	1.4
$\mathbf{D_8}$	2nd heating cooling	g 17.5 Cr 79.7 (141.4) I I 64.1 (11.2) N 28.2 (18.2) Sm$\tilde{C}$	1.4
$\mathbf{D_{16}}$	2nd heating cooling	g 17.6 Sm$\tilde{C}$ 38.5 (34.0) N 65.1 (26.3) I I 64.8 (14.0) N 31.6 (30.0) Sm$\tilde{C}$	0.9
$\mathbf{D_{32}}$	2nd heating cooling	g 15.1 Sm$\tilde{C}$ 44.2 (79.2) N 65.0 (39.3) I I 64.7 (33.9) N 36.4 (80.6) Sm$\tilde{C}$	1.1
$\mathbf{D_{64}}$	2nd heating cooling	g 11.0 Cr 63.7 (415.0) I I 61.0 (69.5) N–[b] Sm$\tilde{C}$	1.1

[a] Enthalpy of the isotropic to nematic transition per mesogenic unit.

[b] Transition detected only by XRD.

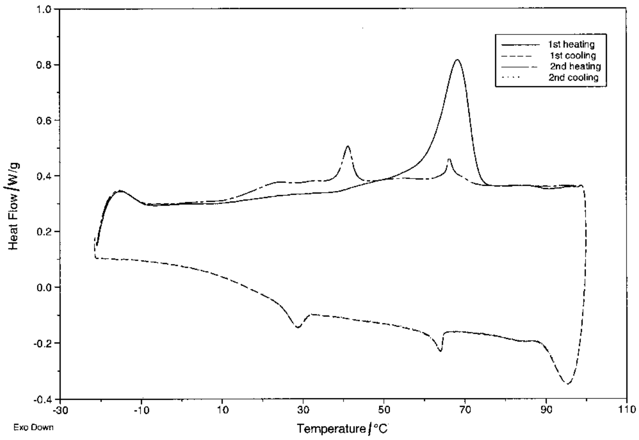


Figure 2. DSC heating and cooling cyles for compounds $\mathbf{D_{16}}$.

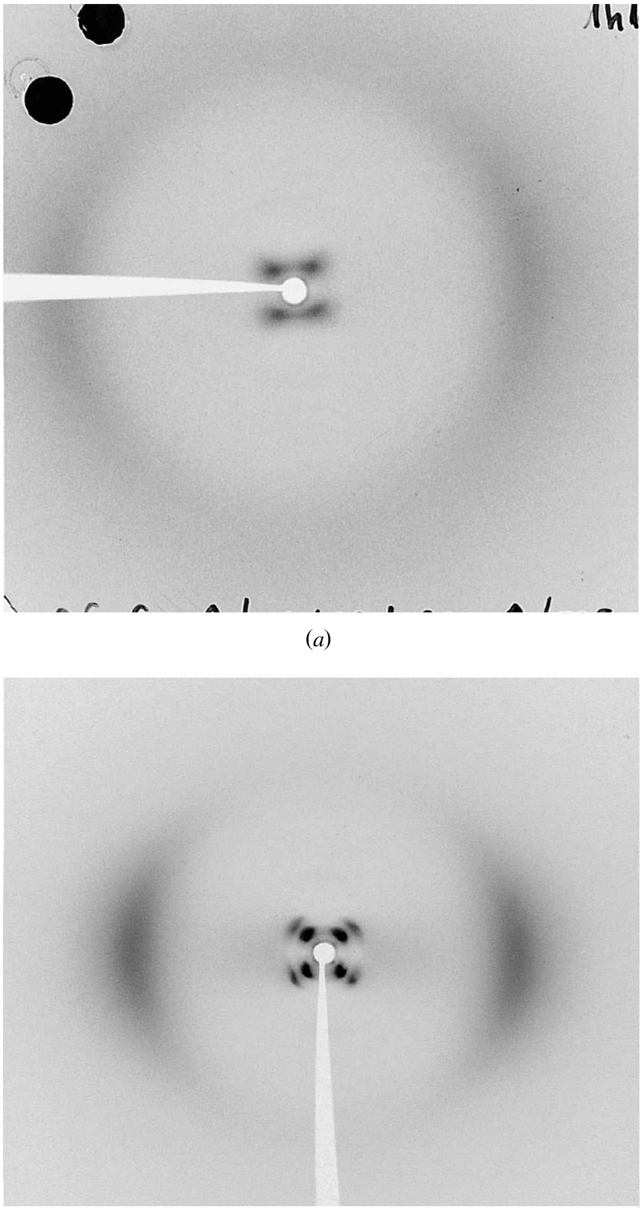
compounds. For example, compounds $\mathbf{D_4}$, $\mathbf{D_8}$ and $\mathbf{D_{64}}$ displayed a glass transition, a cold crystallization and then melted directly to the isotropic liquid. In contrast, $\mathbf{D_{16}}$ and $\mathbf{D_{32}}$ did not crystallize under the conditions in the DSC apparatus or in the hot stage of the microscope, and they showed a glass transition a Sm$\tilde{C}$ to nematic and a nematic to isotropic liquid transition.

All the dendrimers show nematic phases with similar clearing points in all generations (see cooling cycle data in table 1). The enthalpy of the nematic to isotropic liquid transition per mesogenic unit is about the same order of magnitude (1–1.4 kJ mol^{-1}) for all the compounds; therefore interactions between mesogenic units are similar regardless of the number of units present in the molecule or the size of the DAB core. This suggests that the behaviour of these compounds is mainly driven by the mesogenic units and is independent of the generation number.

3.2. *X-ray diffraction studies*

The nematic nature of the high temperature mesophase found in the five dendrimers was demonstrated by XRD. In all cases, the powder pattern consists of two diffuse haloes, one of which is in the small angle region and the other in the large angle region. Such an X-ray pattern is typical of a nematic mesophase. The absence of sharp maxima is due to the lack of long range positional order, whereas the diffuse maxima are related to short range correlations. Only short exposure patterns could be obtained because of the tendency of these compounds to crystallize after several minutes in the nematic mesophase.

Patterns from oriented samples of the nematic mesophases were difficult to obtain due either to the monotropic nature of this mesophase or to the short temperature range in which it is thermodynamically stable. However, we were able to obtain short exposure patterns from some samples that were spontaneously oriented upon cooling from the isotropic liquid (flow-induced orientation). In the oriented patterns, figure 3 (*a*), the large angle halo is split into two diffuse crescents that are centred in the equatorial plane (the plane perpendicular to the alignment direction). This scattering corresponds to a mean distance of about 4.3–4.4 Å and arises from short range correlations between neighbouring mesogenic units, dendrimeric chains and hydrocarbon tails. The fact that this scattering occurs in the equator indicates that the molecules are preferentially aligned along the meridian—vertical direction in figure 3 (*a*). The low angle scattering is observed as diffuse spots close to the meridian (alignment direction), but reinforced at both sides of this direction, thus generating a four-spot pattern. The presence of these off-meridian spots suggests that the nematic mesophase contains local smectic C fluctuations (skewed cybotactic groups).



(*a*)

(*b*)

Figure 3. X-ray diffraction patterns of (*a*) the nematic mesophase of compound $\mathbf{D_{16}}$, (*b*) the modulated Sm$\tilde{C}$ mesophase of compound $\mathbf{D_8}$. Molecules are aligned in the vertical direction.

In agreement with the existence in the cooling scans of a DSC peak at the lower temperature limit of the nematic mesophase, the X-ray experiments reveal the existence of an additional liquid crystal phase below the nematic mesophase in all five compounds. The patterns obtained from non-oriented samples are qualitatively very similar: they consist of two sharp rings in the small angle region and a diffuse halo in the large angle region. This indicates unambiguously the existence of a structural change that is not accompanied by any evident change in the texture by POM. The two low angle spacings (table 2) are neither in the reciprocal ratio 1 : 2, which could indicate a simple lamellar structure, nor in the reciprocal ratio $1:\sqrt{3}$, which could indicate a hexagonal structure. Given the calamitic structure of the mesogenic units attached to the dendrimeric and central moiety, the mesophase might well be lamellar with a ribbon-like structure (i.e. an antiphase) [16].

With the aim of verifying this hypothesis, X-ray patterns were obtained from mechanically aligned samples. A good degree of alignment was achieved for some compounds ($\mathbf{D_8}$, $\mathbf{D_{16}}$ and $\mathbf{D_{32}}$) by scratching with a glass or metal rod the inner wall of the capillaries containing the samples upon cooling from the isotropic liquid to the mesophase, figure 3 (*b*). The diffuse crescents centred in the equator indicate that the molecules are oriented along the stretching direction. In addition to this, each of the low angle maxima condense into an off-meridian four-point pattern which indicates that these maxima correspond to long range correlations that are neither in the meridional nor in the equatorial direction. Furthermore, the two spots observed in each quadrant are not in the same direction (the azimuthal angles of the two sets of maxima are not the same). This fact rules out the possibility that the two maxima correspond to different orders of the same reflection, but is consistent with the ribbon-like smectic structure reported in the literature for other kinds of liquid crystals [16]. It is interesting to note that in each case the smaller angle spot is observed in approximately the same place as the diffuse spot observed in the nematic mesophase of the same compound (d_1 spacing in table 2). The aforementioned features of the X-ray patterns of the low temperature phase are all consistent with a ribbon-like smectic structure in which the molecules are arranged into parallel ribbons or columns with a smectic C-like order

Table 2. X-ray data for the mesophases of compounds $\mathbf{D_4}$–$\mathbf{D_{64}}$. Parameters d_1 and d_2 are the two observed Bragg spacings.

Compound	Mesophase	$T/°\mathrm{C}$	$d_1/\text{Å}$	$d_2/\text{Å}$
$\mathbf{D_4}$	N	50	32.5 (diffuse)	–
	Sm$\tilde{C}$	r.t.	31.4	18.7
$\mathbf{D_8}$	N	40	32.5 (diffuse)	–
	Sm$\tilde{C}$	r.t.	32.3	20.0
$\mathbf{D_{16}}$	N	50	33.5 (diffuse)	–
	Sm$\tilde{C}$	r.t.	32.9	20.6
$\mathbf{D_{32}}$	N	50	35 (diffuse)	–
	Sm$\tilde{C}$	r.t.	33.6	21.4
$\mathbf{D_{64}}$	N	60	33 (diffuse)	–
	Sm$\tilde{C}$	r.t.	35.4	23.3

within the columns. The ribbons are packed into a two-dimensional oblique lattice. The oriented patterns therefore confirm that the low temperature phase is a modulated Sm$\tilde{\mathrm{C}}$ mesophase (also called Sm$\tilde{\mathrm{C}}$ *antiphase*) [16], whereas the high temperature mesophase is nematic with cybotactic SmC-like local domains.

4. Conclusions

We have shown that it is possible to generate nematic mesophases at low temperatures in DAB-derived dendrimers by anchoring suitable mesogenic units in a transverse manner. This method provides a convenient approach to obtaining low viscosity dendrimeric materials.

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