Dendritic nanodevices

Structure-mesomorphism relationship in terminally functionalised liquid crystal dendrimers

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Abstract

We have carried out a study on the supramolecular liquid crystal organisation shown by LC dendrimers. This study has allowed us to draw interesting conclusions about the molecular plasticity of this type of dendromesogens and even to predict the mesogenic behaviour of higher generations of homologous dendrimers or similar dendrimeric structures. Commercial dendrimers (PAMAM and DAB) have been functionalised at the periphery with mesogenic units containing different structural features, namely the number of terminal alkyloxy chains and the position of attachment of the mesogenic units to the dendrimeric core. The mesomorphism of these materials depends on the mesogenic structure. Nematic, smectic and columnar mesophases have been obtained. ***To cite this article: M. Marcos et al., C. R. Chimie 6 (2003).***

Keywords: dendrimers; liquid crystals; dendromesogens; supramolecular organisations

1. Introduction

Research on dendrimeric materials has experienced an outstanding development during the last years, especially within the framework of two fundamental subjects: Polymer Chemistry [1,2] and Supramolecular Chemistry [3]. The promising applications, some of them already a reality, of dendrimers in a very wide range of disciplines such as Medicine [4–6], Pharmacy [4–6], Catalysis [7], etc. have brought about this extraordinary development.

One of the most interesting aspects in Polymer Chemistry is to observe how very weak intermolecular interactions, namely van der Waals forces or, in some cases, intermolecular hydrogen bonding, can determine the unique properties of these materials [2]. This type of studies can be satisfactorily carried out on dendrimers. In these covalent materials, the molecules are forced to adopt very constrained and regular structures and consequently, the different molecular parts tend to adopt the most favourable positions in order to obtain the most stable structure. In this way, dendrimers show a wide variety of macromolecular structures that give rise to original organisations in some cases and/or new and interesting properties in other [2, 8–11].

In connection with Supramolecular Chemistry, liquid crystal dendrimers constitute one of the most significant and original matters of the liquid-phase occurring phenomena [12,13]. In 1992 Virgil Percec

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described the first examples of LC dendrimers [14]. LC dendrimers or dendromesogens (in words of G. Lattermann [15]) have shown to be especially relevant for studies about the structure–liquid crystal activity relationship. In these compounds, the interaction between the mesogenic units can modify the molecular arrangement to a great extent, and consequently the type of mesophase observed, the properties and the potential applications [8,10].

There are two general approaches to the synthesis of this type of materials. The first one consists in the formation of macrostructures with a regular structural growth [16–19]. In the case of LC dendrimers, the mesogenic units are successively introduced within the branches in each dendrimer generation. Some examples of this synthetic approach can be found in the works published by Tomalia [20], Ringsdorf [21] and Percec [14,18,22], in which several series of hyperbranched polymers, based on flexible polyfunctionalised mesogens are reported. The ability of such macromolecules to fold into an anisotropic shape gives rise to the appearance of a nematic liquid crystalline order (Fig. 1).

The second synthetic approach is based on the functionality of the dendrimer terminal groups, which are able to react with molecules incorporating specific functions, i.e. mesogenic units. Therefore, this ap-
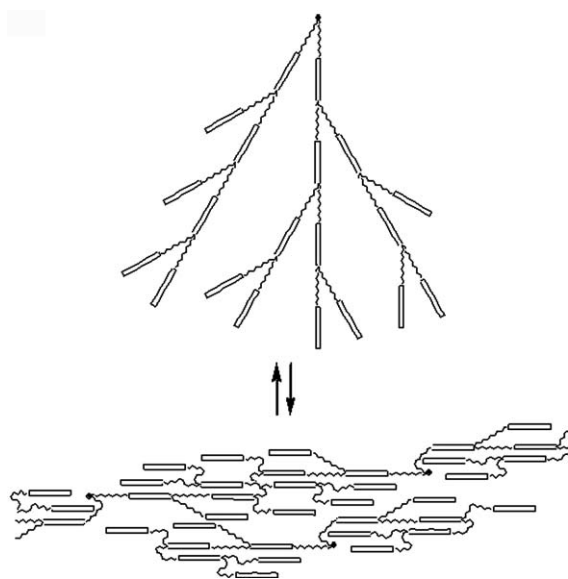
proach allows us to modulate the properties of the dendrimer derivatives. In this sense, it is possible to obtain dendritic architectures that display liquid crystal properties, by the introduction of rod-like [12,23–27] or disk-like [12,28,29] mesogenic units at the periphery of the original dendrimer, forming in this way a liquid crystal shell around the central nucleus (Fig. 2).

During the last years, our group has intensively worked on dendromesogens synthesized according to the second approach. We have reported on the synthesis and liquid crystal properties of several new series of dendrimers derived from poly(amidoamine) (PAMAM) [30–32] and poly(propyleneimine) (DAB) [32–34] dendrimeric cores.

This type of LC dendrimers combines two opposite tendencies: the structural anisotropic units on one side and the isotropic dendritic architecture on the other. On one hand, the branches radiate from a central core becoming more crowded as they extend out to the periphery, resulting in a spherical morphology (starburst shape in dendrimer terminology) i.e. all the branches tend to be isotropically distributed in space because of entropic forces. On the other hand, mesogenic groups are subjected to strong anisotropic interactions with the result of the formation of mesophases owing to the enthalpic gain. Therefore, this class of materials represents a nice example of the competition between entropy and enthalpy within one molecule.

Our main objective is the study of dendrimers as a way to increase our knowledge about the structure – activity relationship in liquid crystals. Three facts hold this purpose:

- (*i*) ease of obtaining both homo- and copolymers;
- (*ii*) the mesogenic units are forced to remain in neighbouring positions, within the dendrimeric structure;
- (*iii*) possibility to favour or disfavour the effect referred in (*ii*) by controlling the phenomenon of microsegregation.

In this study, several mesogenic units have been selected. Most of them derive from 4–(mono–, di– or trialkyloxybenzoyloxy)salicylaldehyde, which are condensed with the terminal amino groups of the corresponding PAMAM and DAB generation. Five generations of LC dendrimers have been synthesized, bearing 4, 8, 16, 32 and 64 mesogenic units respectively (Fig. 3).

Fig. 1. Liquid crystalline hyperbranched polymers and a representation of the molecular anisotropic structure in the nematic phase.
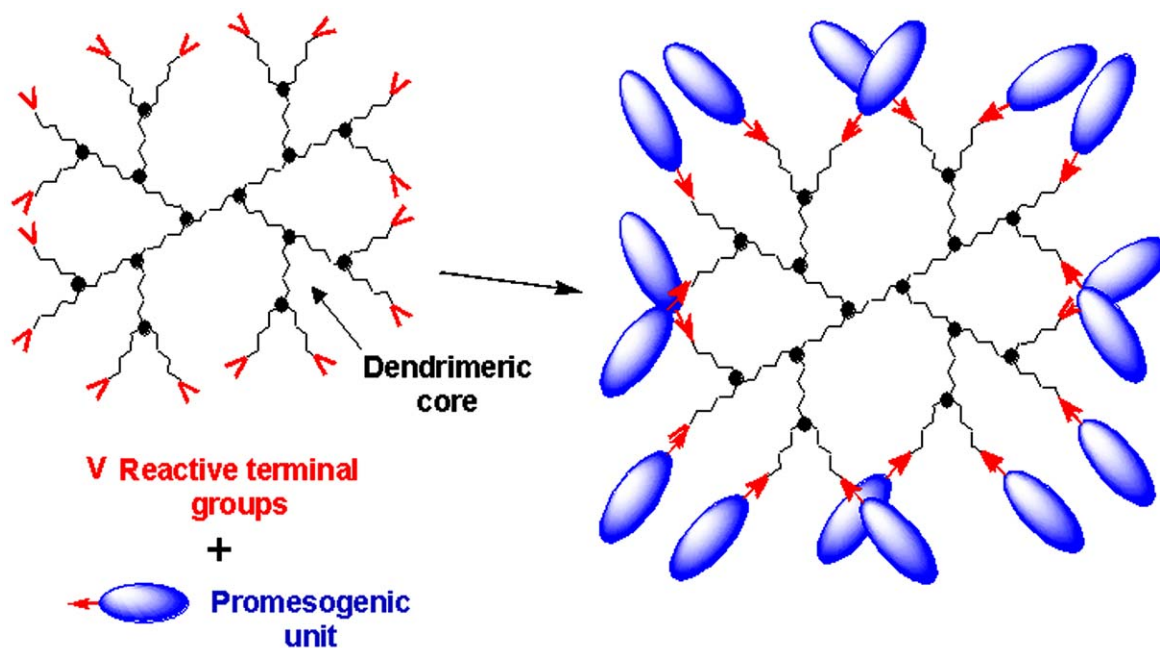
Fig. 2. Dendrimers functionalised with mesogenic units at the periphery.

Another work is based on a family of dendrimers in which mesogenic units with three benzene rings are laterally attached to the dendrimeric core via amido linkages.

The structure of the dendrimers presents three regions with very diverse characteristics (Fig. 4).

(a) The central dendrimeric core as a flexible part in both PAMAM and DAB derivatives. The main differences between both structures are the length of the branches and the possibility of intra– and intermolecular H–bonding due to the amido groups in the case of PAMAM.

(b) The mesogenic units constitute the rigid part of the dendrimer. Their mutual interactions will influence the mesogenic behaviour of the material. In our work, we have chosen typical structures with two or three aromatic rings connected by central ester linkages. The mesogenic units are attached to the dendrimeric core via imino or amido linkages.

(c) The terminal flexible chains, whose length, chirality and number will determine the type of mesophase (as for low molecular weight mesogens). Taking into account the decisive influence of all these three factors, several series of dendrimers including various number (one, two or three) and type (chiral and achiral) of terminal chains have been synthesized.

2. Synthesis and characterisation

The dendrimers are synthesized by the condensation of 4-(mono-, di- or tridecyloxybenzoyloxy) salicylaldehyde with the terminal amino groups of the corresponding generation of PAMAM (0,1,2,3 and 4) or DAB (1,2,3,4 and 5), with the resulting imino linkages between the dendrimeric core and the mesogenic units. The reason for the election of such a mesogenic unit is the presence of a hydroxyl group in position 2 of the benzene ring bearing the aldehyde. In this way, the resulting imine is stabilized by an intramolecular H-bond between the nitrogen atom and the hydrogen of the hydroxyl group. It is well known that the condensation reaction between amines and aldehydes occurs with very high yields in soft reaction conditions. This fact assures an optimal synthetic result, especially when a large number of transformations are involved, i.e. in the case of a high generation dendrimers. All the compounds are isolated as air-stable yellow solids that
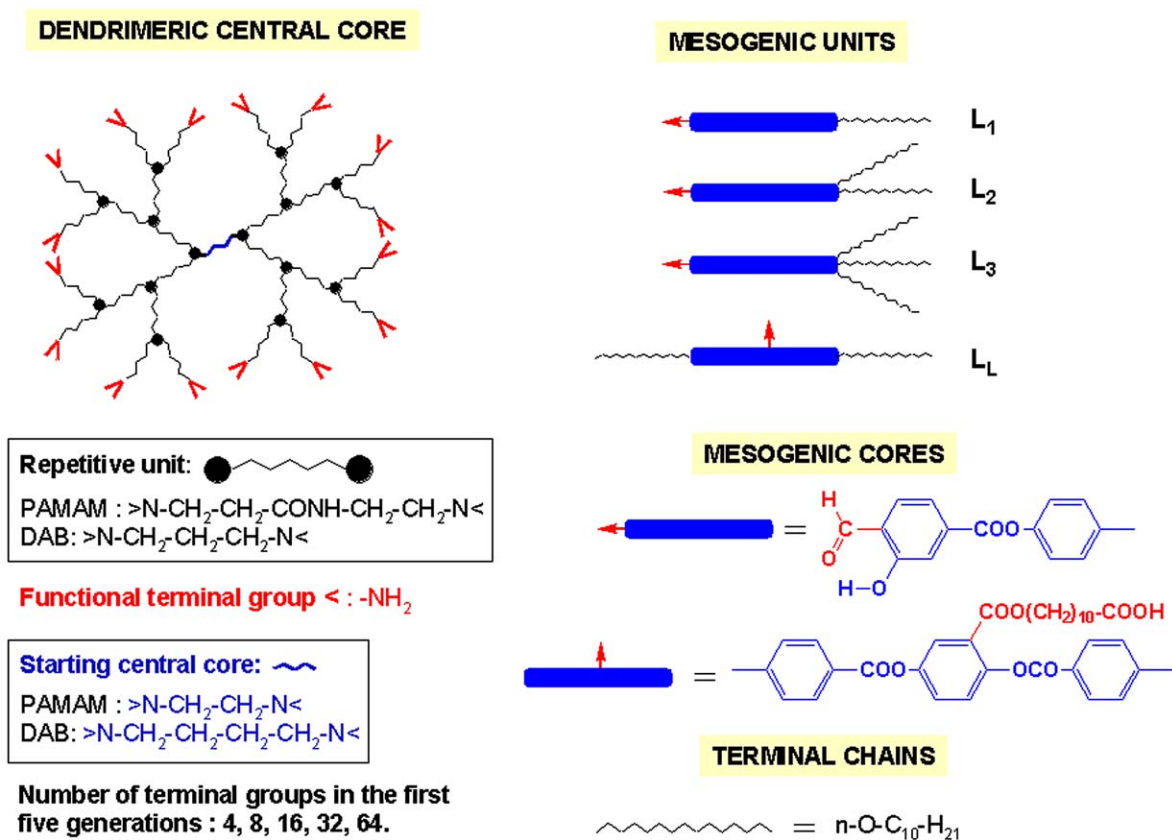
Fig. 3. Schematic view of all the LC dendrimers described in this work.

are soluble in solvents such as dichloromethane, chloroform and THF, and are insoluble in ethanol.

The chemical structures of the dendrimers are established on the basis of ^{1}H NMR, ^{13}C NMR and IR spectroscopy, FAB[+] and MALDI–TOF mass spectrometry, gel permeation chromatography (GPC), and elemental analysis. IR, ^{1}H NMR and ^{13}C NMR spectroscopy have proved very useful in confirming the structure and the purity of these materials. Evidence for the condensation reactions is provided by the lack of a signal at $\delta = 195$ in the ^{13}C NMR spectra (which corresponds to the carbonyl group of the aldehyde) along with the total absence of the NH_2 signals from the starting dendrimer in the ^{1}H NMR and IR spectra. In addition, the excellent solubility of these dendrimers in $CDCl_3$ allowed us to integrate the different peaks in the ^{1}H NMR spectra, confirming in all cases that the expected polymer had been obtained.

3. Mesogenic properties

3.1. Dendrimers with terminally grafted mesogens

Figs. 5 and 6 gather the mesogenic properties of PAMAM and DAB derivatives bearing mesogenic units with one and two terminal alkoxy chains. As it can be seen in the graphs, dendrimers with one-terminal-chain mesogenic units display nematic and smectic mesophases, whereas the homologues with two terminal chains show a hexagonal columnar mesophase.

The mesomorphic behaviour of all the five generations of PAMAM dendrimers is quite similar and consists in the existence of a glass transition between 62 and 67 °C and a smectic A (SmA) mesophase over a wide range of temperature.

Taking into account that the SmA phase is typical of elongated molecules, two questions arise: what is the

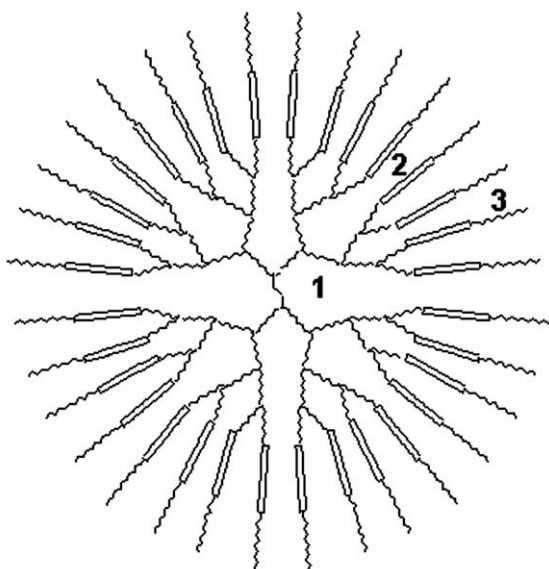Fig. 6. Mesomorphic properties of the dendrimer series DAB $[L_2]_n$ and PAMAM $[L_2]_n$.

Fig. 4. Schematic representation of three diverse regions in a dendrimer:
- (1) central dendrimeric core, as flexible part;
- (2) mesogenic units, as rigid part;
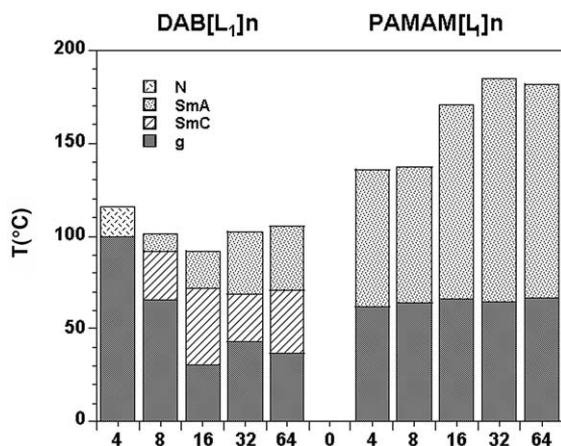- (3) terminal alkyloxy chains.

Fig. 5. Mesomorphic properties of the dendrimer series DAB $[L_1]_n$ and PAMAM $[L_1]_n$.

preferred molecular conformation and what is the nature of the molecular packing in the mesophase?

We have proposed a model in which the flexible poly(amidoamine) chains would adopt the appropriate conformation as to allow the mesogenic units to be parallel to each other, probably extending up and down
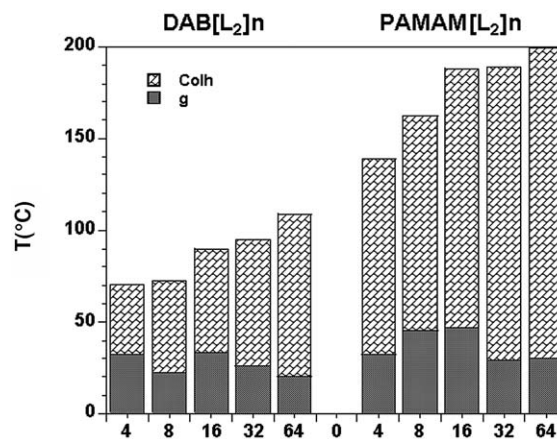
from the molecule centre (see model for PAMAM dendrimer bearing 32 mesogenic units in Fig. 7).

This model would easily explain the mesogenic behaviour of these PAMAM derivatives because the dendrimeric supermolecules can be considered as super-rods that would be ordered parallel to each other promoting the supramolecular order typical of the SmA mesophase. Similar models have been proposed by Meijer [26] and Shibaev [35].

X-ray diffraction (XRD) measurements would provide an additional support to the proposed model if we studied a graphical view of the evolution of the measured layer spacing, which in a SmA mesophase should correspond to the molecular length, upon increasing the generation number (see Fig. 7). Although we assume a cylindrical model as the simplest structure, this molecular model will be deformed in the mesophase in order to fill the space between neighbouring molecules. The increase observed in the layer spacing from PAMAM-L_4 to PAMAM-L_8 is associated with a preferentially extended conformation of the amidoamine moiety. The increase in molecular length is smaller from PAMAM-L_8 to PAMAM-L_{16}, and finally it becomes very small for the highest generation derivatives. In this case, the poly(amidoamine) core tends to fill all the space in the central part of the molecule, meaning that it must adopt a very curled arrangement, and therefore it contributes mainly to the molecular width rather than to the molecular length. This compact conformation of the central dendrimeric
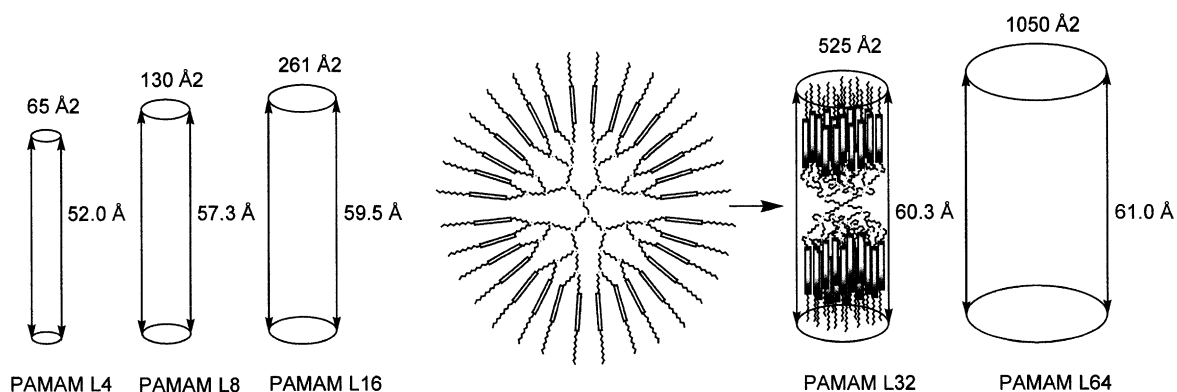
Fig. 7. Schematic view of the parallel arrangement of the mesogenic units in a cylindrical shape, and evolution of the molecule size versus the generation number in PAMAM derivatives.

core is favoured by intramolecular H–bonds between the amido groups.

Even though higher generations (> 5) have not been synthesized, it would be possible to extrapolate the results obtained and expect a similar behaviour. From these data, we could deduce that the dendrimer with 128 mesogenic units might be represented as a cylinder with its height larger than its width. On the contrary, for the next generation dendrimer this trend would be inverted.

One of the most interesting data observed in these models is the additive effect of the mesogenic units. These mesogenic units can be considered as cylinders of a fixed size that are ordered parallel to each other giving rise to a larger cylinder which includes the whole dendrimeric macromolecule. Considering the layer spacing measured by XRD and a density of 1 g cm^{-3}, the calculation of the cylinder base area is straightforward (see Fig. 8). If this calculated area is divided by half the mesogenic units in the dendrimer, the result shows that each mesogenic unit occupies an area of 32–33 Å^2 (in our model half of the mesogenic units are statistically situated up and down the central dendrimeric unit).

DAB dendrimers show a richer mesomorphic behaviour than PAMAM ones, since they show a nematic mesophase and a monotropic smectic C for the dendrimer with four mesogenic units and an smectic A and smectic C polymorphism for the following generations. This significant difference in the mesogenic behaviour can only be attributed to the diverse dendrimeric core. DAB dendrimers differ from PAMAM ones in two main aspects: the length of the branches (four links instead of seven) and the absence of amido groups. This fact is very important since the impossibility of H–bonding within the branches will favour the conformational freedom of the dendrimeric core.
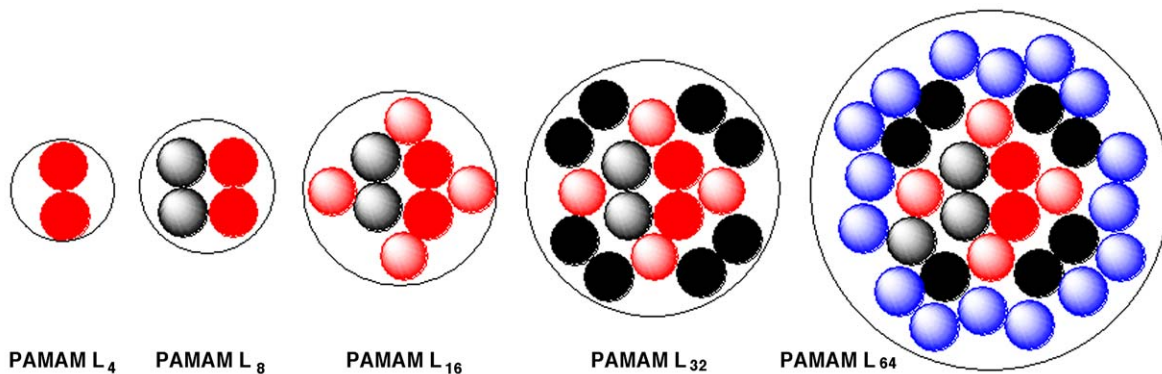

Fig. 8. Schematic representation of the cylinder base area occupied by half of the mesogenic units.
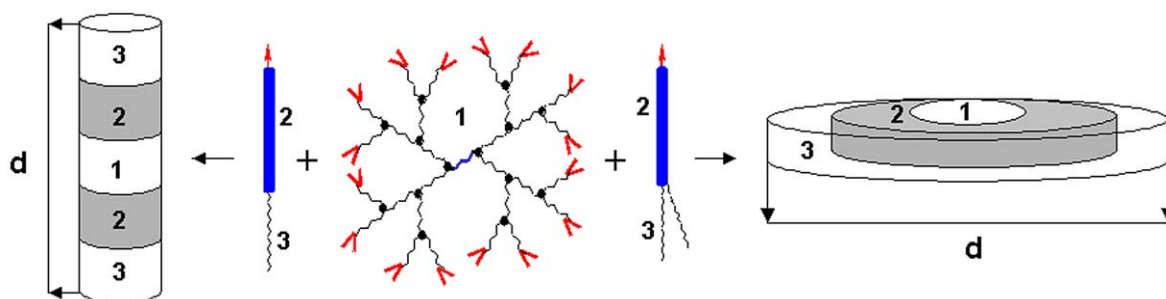
Fig. 9. Schematic representation of the two molecular conformations (parallel and radial) of end-functionalised LC dendrimers depending on the number of terminal alkoxy chains.

As for the PAMAM derivatives, DAB dendrimers show a glassy state at low temperatures. However, the glass transition temperatures depend largely on the generation. The differences observed in the mesogenic behaviour of this series with respect to the previous one are due to the modification of the balance existing between the three regions of the dendrimer (central part, mesogenic units and terminal chains). In this case, both the molecular interactions within the central dendrimeric core and its size are diminished with regard to PAMAM derivatives, therefore the contribution of the mesogenic units becomes more significant and the mesomorphic behaviour resembles that of the low molecular weight derivatives with a similar structure, which show nematic and SmC mesophases [36].

The model proposed for PAMAM dendrimers is also applicable to DAB dendrimers.

Dendrimers incorporating mesogenic units with two terminal chains exhibit a hexagonal columnar mesophase for the five generations under study (Fig. 6). As for dendrimers with one-terminal-chain mesogenic units, PAMAM derivatives show mesogenic ranges much wider than their DAB homologues.

This is another example of the importance of the balance between the three regions of the dendrimer, in this case clearly favourable to the exterior paraffin shell. These dendrimers cannot be arranged in a cylindrical model as that proposed for the smectic phases since the volume of the terminal chains is larger than the area occupied by the mesogenic units. In order to accommodate the terminal chains in such a model, a significant enlargement of the cylinder base should occur, which would cause a diminishment of the interactions within the rigid parts of the mesogenic units and the appearance of holes in the central dendrimeric part. In Supramolecular Chemistry it is well known that "Nature avoids emptiness" and for this reason, dendrimers tend to adopt a diverse conformation so that the mesogenic units can be optimally accommodated. The dendrimer adopts a disk-like radial arrangement, which allows the filling of the space in all its three regions (Fig. 9).

Theoretical calculations on the basis of XRD measurements allow us to determine the number of molecules required to complete a disk (slice) within the column. Considering a disk thickness of 4.6 Å, according to the distance measured in the diffuse scattering halo in the wide angle region which corresponds to the liquid-like disorder of the molten chains, the calculations lead to the following results: approximately 26–27 terminal chains per disk for the first generation (4 mesogenic units) and between 30 and 36 terminal chains for higher generations. Consequently, the number of molecules per disk in each generation is about 3.2 for DL_4, 2 for DL_8, 1 for DL_{16}, 0.5 for DL_{32} and 0.25 for DL_{64}. This means that in the first generation three molecules are needed to fill the hypothetical disk. The arrangement proposed in two extreme models is shown in Fig. 10. Logically, molecules can adopt conformations halfway between the two models. The second generation would require two molecules to fill the disk, represented also as two extreme models in Fig. 10. Just one molecule of the third dendrimer generation would be enough to fill the disk. Finally, molecules of generations 4 and 5 occupy two and four disks respectively. All these supermolecules are arranged in superior supramolecular organisations which give rise to the columns and therefore to the hexagonal columnar mesophase, as it occurs for micellar phases.
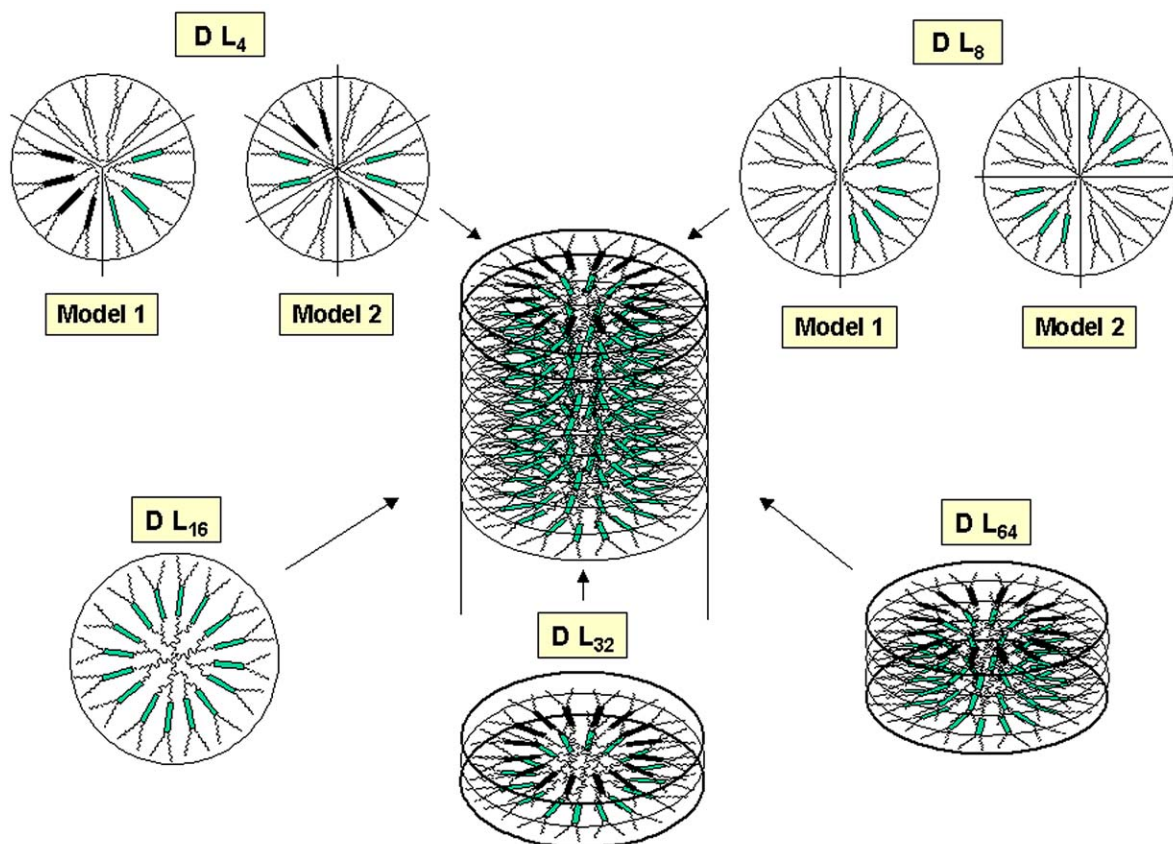
Fig. 10. Schematic representation of the self-assembly process of dendrimers into columns.

3.2. Codendrimers with terminally grafted mesogens

This drastic modification in the mesogenic behaviour with the number of terminal chains in the mesogenic unit (especially PAMAM derivatives that only exhibit a SmA phase or a hexagonal columnar phase when one or two terminal chains are present respectively) led us to the study of some intermediate states in order to better understand the evolution from lamellar to columnar mesophases. To achieve this purpose a series of codendrimers was synthesized, in which both mesogenic units (one- and two-terminal chains) were introduced in various proportions (Fig. 11).

The synthesis of these codendrimers was carried out by reaction of a mixture of the two mesogenic units in the appropriate proportions with the terminal amino groups of the PAMAM generation bearing 32 terminal units. The characterisation of the codendrimers using ^{1}H and ^{13}C NMR spectroscopy allows us to prove that the statistically ratio of the mesogenic moieties in the
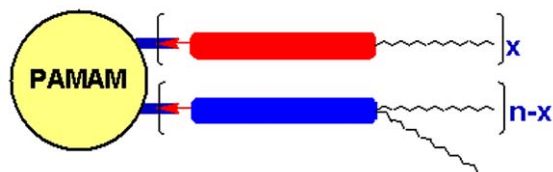

Fig. 11. General structure of LC codendrimers.

codendrimers is in excellent agreement with the proportion of comonomers in the condensation reaction.

The mesomorphic behaviour of some of the codendrimers synthesized is represented in Fig. 12.

As it can be seen, the introduction of a small content of the two-terminal-chain comonomer leads to the appearance of the SmC phase below the SmA phase, whereas larger contents of this comonomer favour the occurrence of a rectangular columnar mesophase. As expected, the central dendrimeric core is not able to accommodate all the mesogenic units and their termi-
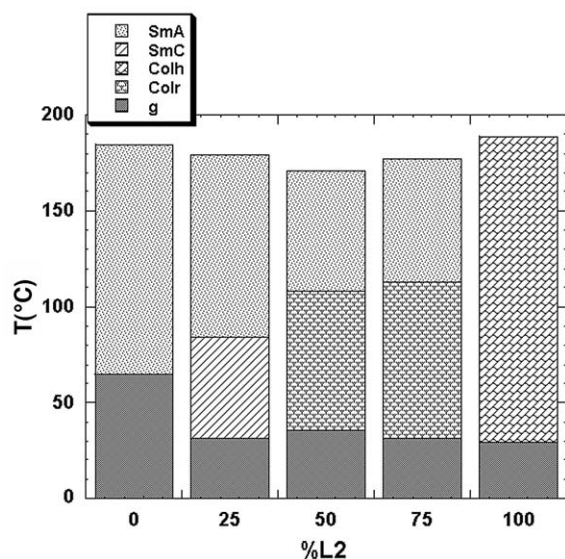
Fig. 12. Mesomorphic properties of LC codendrimers as a function of L_2 (two-terminal-chain mesogenic unit) content.

nal chains within the area of the model orthogonal cylinder, since now there are more terminal chains for the same number of mesogenic units. The dendrimeric supermolecule solves this problem by adopting a tilted structure that permits the accommodation of the terminal chains due to its larger area (Fig. 13).

As the number of terminal chains increases, i.e. the content of the two-terminal-chain comonomer increases, the accommodation of the terminal chains within a cylindrical structure becomes unfeasible, and this is deformed to a rectangular parallelepiped superstructure, which at a supramolecular level, gives rise to a rectangular columnar mesophase. The relation between the space required in order to accommodate the terminal chains and the volume of the central dendrimeric core is insufficient to fill all the surrounding space and therefore only when the number of terminal chains
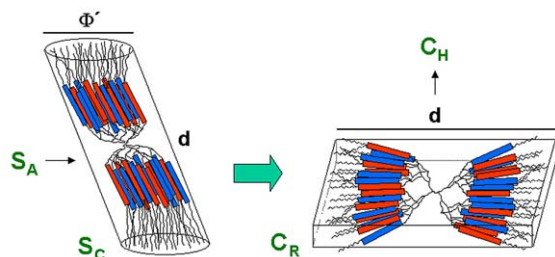

Fig. 13. Schematic representation of the evolution from lamellar to columnar mesophases in LC codendrimers.

is similar to that of the corresponding two-terminal-chain homodendrimer, the relation is such that a hexagonal columnar mesophase is formed.

3.3. Recent works

As a continuation of these studies we are currently working with PAMAM and DAB-based dendrimers in order to obtain cubic phases. A first attempt has been performed using the same mesogenic units bearing three terminal chains (4-(3',4',5'-tridecyloxybenzoyloxy)–salicylaldehyde), however the dendrimers containing 32 and 64 units exhibit only a hexagonal columnar phase in both dendrimers. Nevertheless recent works with DAB dendrimers incorporating complex units, previously described by Percec et al., bearing six and nine terminal chains appear to be very promising as the preliminary polarized microscopic studies is concerned. X-ray diffraction characterisation will allow us to confirm these results.

3.4. Dendrimers with laterally grafted mesogens [34]

Most of the resulting dendrimers derived from PAMAM or DAB formed when the mesogenic units are 4-(mono-, di- or tridecyloxybenzoyloxy)salicylaldehyde (with one exception) exhibit smectic mesophases. 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 that could be obtained if they displayed a nematic mesophase [14,37,38]. Nematic phase is the least viscous LC phase and has 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 chain liquid crystalline polymers [39,40]. 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 a nematic ordering [37,41]. Thus we synthesized a new series of dendrimers derived from poly(propyleneimine) that contain 4, 8, 16, 32, and 64 peripheral laterally grafted mesogenic units attached across and amide linkage to DAB generations 1, 2, 3, 4, 5 (Fig. 3).
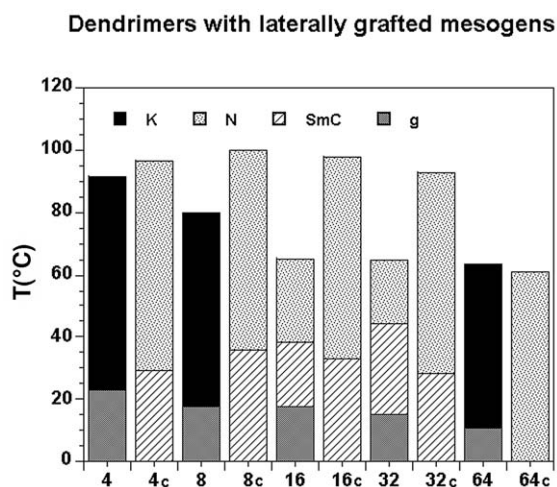
Fig. 14. Mesomorphic properties of dendrimers with laterally grafted mesogens.

The general procedure for the preparation of the liquid crystalline dendrimers was the reaction of the different generations of the $[DAB–(NH_2)_n]$ with an activated ester of the mesogenic unit (the pentafluorophenyl derivative) following a method similar to that described by Meijer et al. [26].

Optical and thermal data for the second heating and cooling processes of the dendrimers are shown in Fig. 14. Compounds **DL_4, DL_8** and **DL_{64}** displayed a glass transition, a cold crystallization and then melted directly to the isotropic liquid. In contrast, **DL_{16}** and **DL_{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 modulated smectic C to nematic and nematic to isotropic liquid transitions. All the dendrimers exhibit a nematic mesophase, which was identified in each case by the *schlieren* texture observed by polarized optical microscopy and at lower temperature they exhibit a SmC modulated mesophase.

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, as it occurs in the homologous series of terminally attached dendrimers. This suggests that the behaviour of these compounds is mainly driven by the mesogenic units and is independent of the generation number.
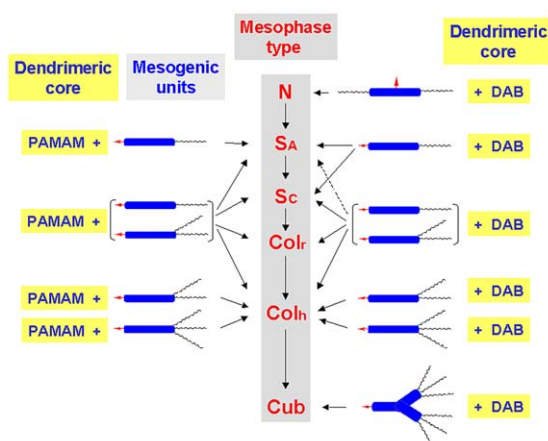

Fig. 15. Obtention of dendrimers with a given mesophase: synthesis 'à la carte'.

In conclusion 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.

4. Conclusions

In this work, we have use the dendrimers as a tool to improve our knowledge on the structure-activity relationship in liquid crystals. Modifying the central dendrimeric core, the mesogenic units and the peripheral chains we have succeeded in obtaining dendrimers with a given mesophase: synthesis 'à la carte' (Fig. 15).

Acknowledgements

References

[1]   J.M.C. Cowie, Polymers Chemistry and Physics of Modern Materials, International Textbook Company Limited, Aylesbury, 1973 Bucks HP20 ITL.

[2] F.W. Billmeyer Jr, Textbook of Polymer Science, 3rd ed., Wiley Interscience, New York, 1984.

[3] J.M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304.

[4] N. Ardoin, D. Astruc, Bull. Soc. Chem. Fr. 132 (1995) 875.

[5] A.W. Bosman, H.M. Janssen, E.W. Meijer, Chem. Rev. 99 (1999) 1665.

[6] A. Archut, F. Vögtle, in: H.S. Nalwa (Ed.), Handbook of Nanostructured Materials and Nanotechnology, Vol. 5: Organics, Polymers and Biological Materials, Academic Press, New York, 2000.

[7] D. Astruc, F. Chardac, Chem. Rev. 101 (2001) 2991.

[8] G.R. Newkome, C.N. Moorefield, F. Vögtle, Dendritic Molecules: Concepts, Syntheses and Perspectives, VCH, Weinheim, 1996.

[9] D.A. Tomalia, A.M. Naylor, W.A. Goddard III, Angew. Chem. Int. Ed. Engl. 29 (1990) 138.

[10] O.A. Matthews, A.N. Shipway, J.F. Stoddart, Prog. Polym. Sci. 23 (1998) 1.

[11] P.R. Ashton, S.E. Boyd, C.L. Brown, S.A. Nepogodiev, E.W. Meijer, H.W.I. Peerlings, J.F. Stoddart, Chem. Eur. J. 3 (1997) 974.

[12] S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev, Polymer Science Ser. C 43 (2001) 1.

[13] J.W. Steed, J.L. Atwood, Supramolecular Chemistry, John Wiley & Sons, Ltd. Chichester, 2000, p. 573.

[14] V. Percec, M. Kawasumi, Macromolecules 25 (1992) 3843.

[15] J.H. Cameron, A. Facher, G. Lattermann, S. Diele, Adv. Mater. 9 (1997) 398.

[16] Y.H. Kim, J. Am. Chem. Soc. 114 (1992) 4947.

[17] V. Percec, M. Kawasumi, Polym. Prepr. 33 (1992) 221.

[18] V. Percec, P.W. Chu, M. Kawasumi, M. Toward, Macromolecules 27 (1994) 4441.

[19] V. Percec, Pure Appl. Chem. 67 (1995) 2031.

[20] S.E. Friberg, M. Podzimell, D.A. Tomalia, D.M. Hedstrand, Mol. Cryst. Liq. Cryst. 164 (1988) 157.

[21] S. Bauer, H. Fischer, H. Ringsdorf, Angew. Chem. Int. Ed. Engl. 32 (1993) 1589.

[22] S.D. Hudson, H.T. Jung, V. Percec, D.W. Cho, G. Johasson, G. Ungar, U.S.K. Balagurusamy, Science 278 (1997) 449.

[23] S.A. Ponomarenko, E.A. Rebrov, A.Y. Bobronsky, N.I. Boiko, A.M. Muzafarov, V.P. Shibaev, Liq. Cryst. 21 (1996) 1.

[24] S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev, R.M. Richardson, I.J. Whitehouse, E.A. Rebrov, A.M. Muzafarov, Macromolecules 33 (2000) 5549.

[25] K. Lorenz, D. Hölter, R. Mühlhaupt, H. Frey, Adv. Mater. 8 (1996) 414.

[26] M.W.P.L. Baars, S.H. Söntjens, S.H.M. Fischer, H.W.I. Peerlings, E.W. Meijer, Chem. Eur. J. 4 (1998) 2456.

[27] S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev, Polymer Science 43 (2001) 1 Ser. C and references therein.

[28] D.J. Pesak, J.S. Moore, Angew. Chem. Int. Ed. Engl. 36 (1997) 1636.

[29] H. Meier, M. Lehmann, Angew. Chem. Int. Ed. Engl. 37 (1998) 643.

[30] J. Barberá, M. Marcos, J.L. Serrano, Chem. Eur. J. 5 (1999) 1834.

[31] M. Marcos, R. Giménez, J.L. Serrano, B. Donnio, B. Heinrich, D. Guillon, Chem. Eur. J. 7 (2001) 1006.

[32] B. Donnio, J. Barberá, R. Giménez, D. Guillon, M. Marcos, J.L. Serrano, Macromolecules 35 (2002) 370.

[33] J. Barberá, M. Marcos, A. Omenat, J.L. Serrano, J.I. Martínez, P.J. Alonso, Liq. Cryst. 27 (2000) 255.

[34] J. Barberá, R. Giménez, M. Marcos, J.L. Serrano, Liq. Cryst. 29 (2002) 309.

[35] R.M. Richardson, S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev, Liq. Cryst. 26 (1999) 101.

[36] J.L. Serrano, P. Romero, M. Marcos, P.J. Alonso, J. Chem. Soc. Chem. Commun. (1990) 859.

[37] I.M. Saez, J.W. Goodby, R.M. Richardson, Chem. Eur. J. 17 (2001) 2758.

[38] V. Percec, P. Chu, G. Ungar, J. Zhou, J. Am. Chem. Soc 117 (1995) 11441.

[39] F. Hessel, H. Finkelmann, Polym. Bull. 14 (1985) 3751.

[40] P. Keller, F. Harduin, M. Mauzac, M.-F. Achard, Mol. Cryst. Liq. Cryst. 155 (1988) 171.

[41] R. Elsäber, G.H. Mehl, J.W. Goodby, M. Veith, Angew. Chem. Int. Ed. Engl. 40 (2001) 2688.