Highly congested liquid crystal structures: dendrimers, dendrons, dendronized and hyperbranched polymers

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In this *tutorial review* we describe some studies concerning liquid crystal dendritic polymers. We have chosen to present several representative examples that illustrate the diverse kinds of LC dendritic structures, namely: dendrimers, dendrons, dendronized polymers and hyperbranched polymers. We review their synthesis, mesogenic properties and the way that they are arranged to form supramolecular liquid crystal assemblies.

Abbreviations

LC	Liquid Crystal
SmA	Smectic A Mesophase
SmC	Smectic C Mesophase
N	Nematic Mesophase
Colr	Rectangular Columnar Mesophase
Colh	Hexagonal Columnar Mesophase
PAMAM	Poly(amidoamine)
PPI	Poly(propylene imine)
PEI	Poly(ethylene imine)
HbLCP	Hyperbranched Liquid Crystal Polymer
(PEIMe)	Methylated Hyperbranched PEI

1 Introduction

Dendrimers constitute one of the most important research topics nowadays, and are of great interest in Materials Science (mainly, in Nanoscience and Nanotechnology), as well as in Biomedical Sciences. Many practical and potential applications have already been found for dendrimers in fields such as health care, engineering, consumer goods, environmental sciences, electronics, optoelectronics, *etc.*[1,2]

Dendrimers and dendrimeric units (dendrons) may be considered as polymers with geometrically-restricted structures, and for this reason they are one of the most versatile, compositionally and structurally controlled synthetic nanoscale building blocks available today. These systems possess a well-defined structure, which allows the control of their size and shape. Additionally, they present very low polydispersities and allow a wide variety of functionalisation of their structures.

Liquid crystal (LC) dendrimers have been investigated since the early 90's, but the most significant development in the research of this topic occurred much more recently.[3] The first studies dealt basically with fundamental research whose main objective was the accomplishment of mesogenic behaviour with dendrimeric structures. After the first steps, the current investigation on LC dendrimers is focused on the search for applications for these materials.

Here we present a tutorial review on the topic, in which the most representative work on each subject will be cited. Many other related studies can be found within the references given.

1.1 Synthesis and structure of liquid crystal dendrimers

LC dendrimers are generally prepared by the introduction of mesogenic units within a dendrimeric structure. The simplest method consists of the attachment of the units to the peripheral functional groups of a conventional dendrimer, as for side-chain polymers (Fig. 1). In this case, the main chain is the dendrimer structure itself. This is the most widely used strategy for the preparation of LC dendrimers by far.

The structure of such side-chain LC dendrimers consists of a flexible branched network with a branching multiplicity N_B which has been grown from a single multivalent initiator core with a connectivity N_C and a number of mesogenic units which are laterally (side-on) or terminally (end-on) attached to the periphery of the dendrimeric network (Fig. 2).

A less employed method to prepare LC dendrimers involves the introduction of the mesogenic groups as the repeating units within the central dendrimer structure, as for main-chain polymers (Fig. 3).

Starting from a preformed dendritic polymer allows the easy preparation of both homo- and codendrimers. One-pot synthetic procedures afford easily random side-chain liquid crystal dendrimers combining two or more different mesogenic units[4]

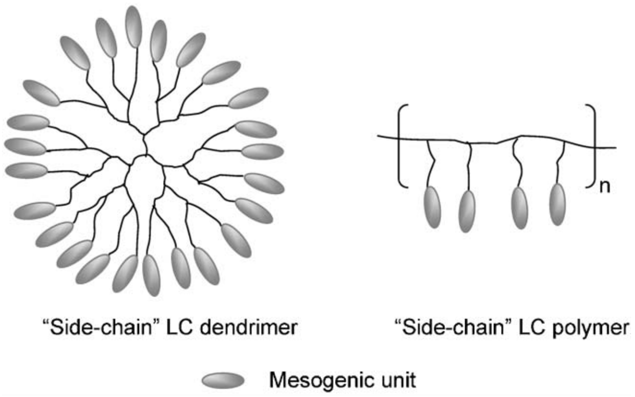

Fig. 1 Schematic structure of "side-chain" LC dendrimers.

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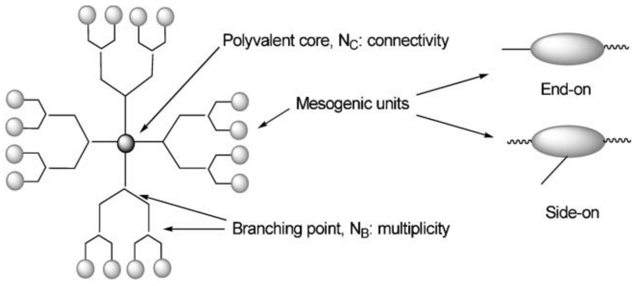

Fig. 2 Schematic parts of a liquid crystal dendrimer.

(Fig. 4). The convergent synthesis of dendrimers is a tool to obtain both side-chain and main-chain block codendrimers (Fig. 5) in which the mesogenic units of each type are not randomly distributed but located at specific sites of the structure.

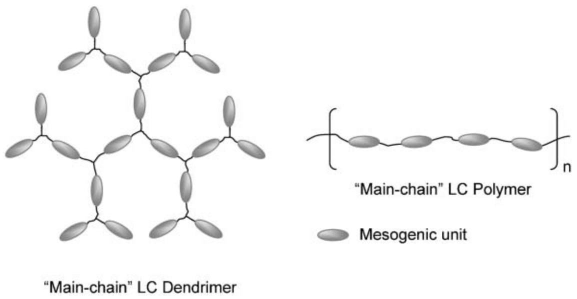

Fig. 3 Schematic structure of "main-chain" LC dendrimers.

In addition to these regular globular structures prepared by a convergent synthetic method, the dendrons used as precursors are, in some cases, mesogenic by themselves.

Mercedes Marcos

Mercedes Marcos was born in 1956 in Zaragoza (Spain). She studied chemistry at the University of Zaragoza. In 1983 she obtained her PhD under the direction of Professor Enrique Meléndez and Professor José Luis Serrano (Department of Organic Chemistry, Zaragoza, Spain). In 1987 she obtained a permanent position as Colaborador Científico at the Consejo Superior de Investigaciones Científicas (CSIC) and since 1993 she has been Investigador Científico of the Instituto de Ciencia de Materiales de Aragón (CSIC – Universidad de Zaragoza). She is interested in the design and synthesis of functional self-assembling systems (ferroelectric liquid crystals, metallomesogens, liquid crystalline dendrimers and dendritic networks). She has published over 100 scientific articles and is co-author of a book on metallomesogens.

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Dr Ana Omenat obtained her PhD degree from the University of Zaragoza, and after working with Prof. Ghedini in the University of Calabria and in Philips Research Laboratories in Eindhoven, she joined the Liquid Crystal Group at the University of Zaragoza. Her research activities have always been related to liquid crystals: low and high molecular weight organic and metallo-organic materials.

José Luis Serrano

José Luis Serrano received his PhD in Chemistry in 1980 from the University of Zaragoza (Spain). In 1996, he obtained the position of Full Professor of Organic Chemistry in the University of Zaragoza. Since 1985 he has belonged to the Institute of Materials Science of Aragón (ICMA), and now he is Vice-Director of the Institute of Nanoscience of Aragón (INA). He is the leader of the CLIP Group (Liquid Crystals and Polymer group), a team of physicists and chemists that has been classified as a Group of Excellence by the Government of Aragón. In recent years Prof. Serrano's research has been devoted to the use of liquid crystals as a tool in supramolecular chemistry, dendrimers and polymers in order to obtain functional materials with relevant optical and electrooptical properties.

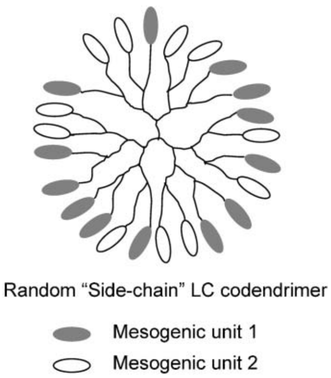

Fig. 4 Schematic structure of ''random side-chain'' LC codendrimers.

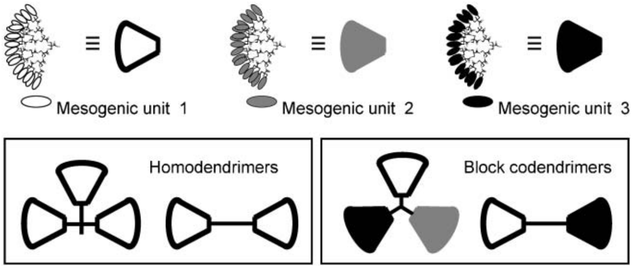

Fig. 5 Schematic structure of ''LC dendrimers based on monodendrons''.

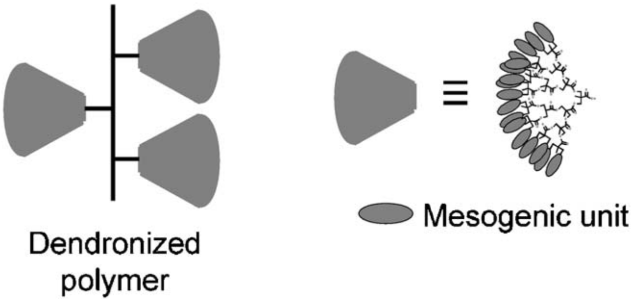

Fig. 6 Schematic structure of ''LC dendronized polymers''.

Such dendrons may be attached to several central structures. In this way, a variety of hybrid and multifunctional materials have been prepared, in which the structural moieties attached to the periphery may tune or modify the properties of the dendrimeric material.

One of the most significant chapters of this review is devoted to the so-called dendronized polymers,[5] in which the dendrons are lateral substituents of main-chain polymers (Fig. 6). In these systems the steric congestion of the dendrons leads to the formation of rigid structures with properties different to those of the polymer in many cases.

In general, the synthesis of dendrimers and dendrons consists of a number of iterative steps and requires an exhaustive purification procedure (*e.g.* column chromatography, recrystallization, extraction or azeotropic distillation). For these reasons, the preparation of dendrimers is tedious and/or complicated and therefore, the final products are quite expensive. Another convenient approach to such systems is the use of hyperbranched polymers.[6] These polymers lack the regularity typical of the dendrimers, but in many cases, present similar properties. Since the preparation of the hyperbranched polymers is easily accomplished and thus they are cheaper than dendrimers, use of this approach can be of great interest for certain applications in which a defined structure or composition is not needed.

Taking into account this classification, in this review, we intend to collect the most significant results reported to date for each type of liquid crystal materials: dendrimers, dendrons, dendronized polymers and hyperbranched polymers (Fig. 7).

2 Liquid crystal dendrimers

In this group we include only those compounds which strictly fulfil the requisites that define a dendrimer.

2.1 Side-chain LC dendrimers

As aforementioned, most of the reported materials correspond to the structure of side-chain LC dendrimers. In this approach, the promesogenic units are grafted onto the periphery of a preformed dendrimer. For this kind of materials, the most used dendrimers have been silicon-containing (siloxanes, carbosilanes and carbosilazanes), poly(propylene imine), poly(amidoamine), and polyester-based dendrimers.

These dendrimers, in particular the higher generations, possess a spherical symmetry. The branches tend to be isotropically distributed in space because of entropic forces. In contrast, the promesogenic units, which are either side-on or end-on attached at the periphery of the dendrimer, strongly interact with each other to give rise to anisotropic mesophases owing to the enthalpic gain, as occurs in conventional liquid crystals. Most often the enthalpy gains over the entropy in the interesting competition between those two tendencies in these systems. This general behaviour has been observed by

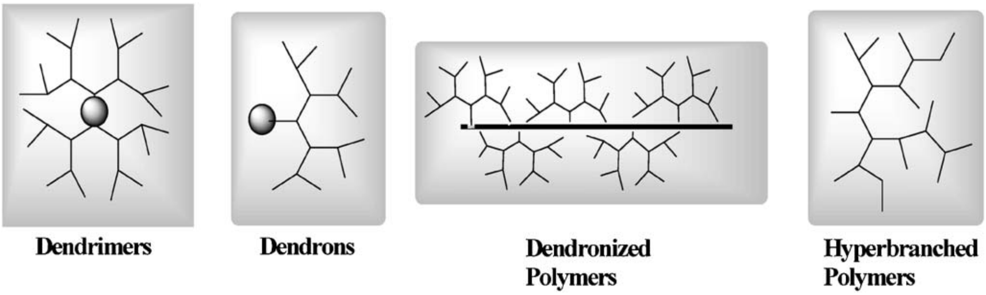

Fig. 7 Dendritic polymer structures.

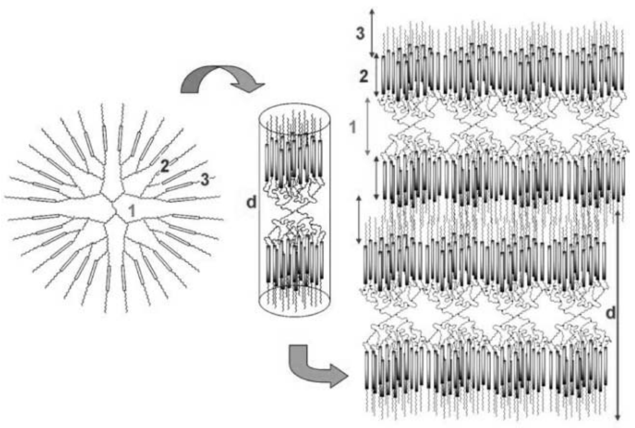

Fig. 8 Schematic representation of the supramolecular structure of the dendrimers in the lamellar mesophase.

numerous authors with a great diversity of dendrimers, showing that the intermolecular interactions among the promesogenic units condition the conformation of the dendrimer, which adapts to their requirements as long as it is conformationally and sterically possible. Thus, the final overall conformation favours the interactions between the mesogenic units and gives rise to the appearance of the liquid crystalline state.

Nematic, smectic and columnar phases have been described for this kind of materials by changing only the number or the length of the terminal chains of the mesogenic units. In this way, the nematic phase has been obtained either by use of side-on attached calamitic units, or by use of end-on attached calamitic units bearing short terminal alkyl chains.[7] The first behave in a similar way to side-chain liquid crystal polymers and in the case of end-on liquid crystal dendrimers the mesogenic behaviour is similar to that of low molecular weight liquid crystals, the nematic mesophase when the terminal chain of the mesogenic unit is short and the smectic one for longer chains.

Numerous examples of LC dendrimers exhibiting lamellar phases have been reported. In most of them, the promesogenic units exhibit end-on linkages and bear long terminal chains or polar groups. To explain the smectic behaviour, a model has been proposed, in which the dendrimeric supermolecule adopts a cylindrical conformation: the dendritic matrix expands in a plane parallel to the smectic layers whereas the promesogenic units are arranged parallel to each other, extending up and down perpendicular to that plane. The number of mesogenic units above and below the dendritic matrix follows statistics, which allows the proposal of an ideal model with an equal number of promesogenic units for each base of the cylinder. The cylinders are arranged parallel to each other giving rise to layered supramolecular organizations, that is, lamellar phases (Fig. 8).

A dendrimeric supermolecule belonging to this group can be divided into three parts: the central dendritic matrix and the terminal chains are very flexible and can be deformed according to the requirements of the promesogenic units, which are located between both of them and arranged parallel to each other so that the interactions are maximized.[8,9]

It has been observed that the layer thickness does not change significantly on increasing the generation of the dendrimer, meaning that only the diameter of the cylinder of the proposed model changes while its height stays nearly constant. This can be explained if the dendritic matrix strongly deforms in the directions parallel to the smectic layers with increasing generation number, allowing more promesogenic units to be accommodated in the cylinder and thus maintaining the lamellar order (Fig. 9).

Logically, the growth of the diameter of the supermolecule has a limit, since the number of promesogenic units grows geometrically whereas the length of the dendritic branches

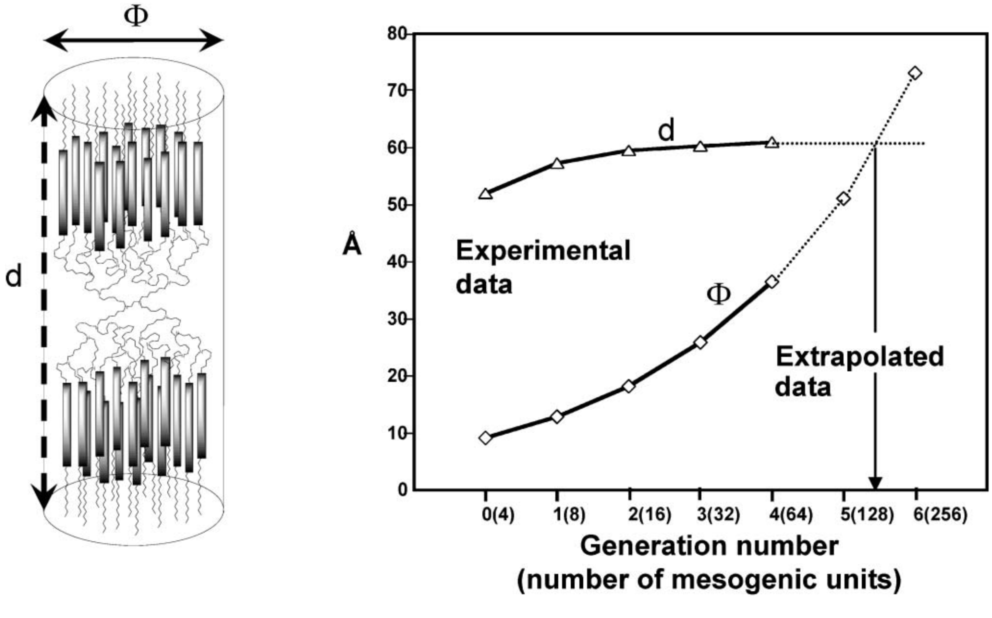

Fig. 9 Graphical representation of the molecule length *d* and the molecule diameter *Φ* *versus* the generation number in PAMAM dendromesogens.

grows linearly as the generation number increases. To avoid exceeding this limit, which is marked by the length of the repeating unit of the dendrimer and the branch multiplicity, the supermolecule undergoes conformational changes, promoting the formation of different phases.

Thus, if we compare the properties of analogous generations of PAMAM and PPI liquid crystal dendrimers bearing *n*-decyloxy terminal chains, we observe that the former exhibit only a smectic A mesophase (orthogonal), whereas for the latter a smectic C mesophase (tilted) also appears.[7] Another example is found in the case of carbosilane LC dendrimers.[10] For low generation numbers, they self-assemble in a SmA phase, but for the fifth generation an additional columnar phase is observed. This phenomenon is explained by taking into account again the great flexibility of the dendritic matrix. The repeating unit of PPI is sensitively shorter than that of PAMAM, and the cylindrical supermolecule tilts so that more mesogenic units can be accommodated while the interactions among them are maintained. The tilt of the cylinder affords a larger area of the ideal cylinder base, which allows the accommodation of a larger number of mesogenic units and terminal chains that would not fit in the orthogonal cylindrical model.

When the tilted cylindrical model is not enough to accommodate all the mesogenic groups, an even more significant change is observed. In this case the supermolecule adopts a disc-shaped conformation leaving more space for the promesogenic units than in the cylindrical model. Columnar phases are formed accordingly as observed for carbosilane LC dendrimers. This phenomenon has been clearly demonstrated with the functionalization of PPI and PAMAM dendrimers with promesogenic units bearing two, three, six and nine terminal chains. All the materials thus obtained exhibit columnar phases explained by a disc-shaped conformation of the supermolecule. In contrast to the lamellar phases, on increasing the generation of the dendrimer the diameter does not change especially but its height increases notably.

The study of codendrimers which contain mesogenic units bearing one and two terminal chains has allowed observation of a sequence of phases SmA → SmC → Colr → Colh as the number of mesogenic units bearing two terminal chains increases.[11]

It must be highlighted that the temperature plays an important role in this behaviour. For instance, in the compounds reported by Shibaev,[10] upon heating the low temperature lamellar phase a columnar rectangular phase appears which finally changes to a columnar hexagonal phase at higher temperatures. A similar effect has been observed in the case of the aforementioned codendrimers derived from PAMAM, in which the SmC and columnar rectangular phases appear below the columnar hexagonal.

The flexibility of the dendritic matrix has also been shown when discotic promesogenic units derived from triphenylene have been attached to its periphery. As a result highly ordered columnar phases have been obtained.

At the same time that these fundamental studies of the structure–activity relationships were carried out, the first work with functional mesogens was started with a view to applications of these materials. The search for ferroelectric properties created by the introduction of chirality in the promesogenic units was one of the first attempts. The work by Busson *et al.*[46] in polyester-based dendrimers and by Shibaev *et al.* in carbosilane dendrimers has been especially relevant in this field. Both groups succeeded in measuring ferroelectric properties for this kind of materials. For example, the studies performed by Shibaev *et al.*[12] conclude that the spontaneous polarization and the tilt angle decrease with an increase of the generation number, whereas the switching time increases. Similar attempts with dendrimers derived from PAMAM and PPI were not successful because the mesomorphic behaviour was lost with the introduction of chiral terminal chains.

This behaviour evidences the importance the central dendrimer has for the properties of the material. Nevertheless, only a few studies of ferroelectric dendrimers have been reported in the last few years, probably due to the high viscosity of these materials in the LC mesophases, which hinders their practical use in favour of low molecular weight molecules.

The capacity of the dendrimers to self-assemble has allowed the design of LC dendrimers without any promesogenic unit. One of the first examples of LC dendrimers was reported by Lattermann *et al.*[13] Different generations of PPI dendrimer were functionalized with 3,4-bis(decyloxy)benzoyl groups *via* amide linkages. The first four generations exhibit LC columnar hexagonal behaviour. In the absence of anisotropic mesogenic units, the microsegregation between polar and apolar regions is the driving force for the formation of the observed mesophase. The dendrimers of different generations behave as cylindrical segments which pile up to give rise to a columnar mesophase (Fig. 10).

The ionic materials are the most interesting example using this approach in LC dendrimers. Some of these compounds have been reported, the most outstanding being those lacking any aromatic moiety. Thus, a number of different mesophases have been observed for ionic derivatives of linear carboxylic acids with PAMAM or PPI dendrimers.[14] Here as well, microsegregation plays a key role and the molecule is divided into three parts which are clearly defined: the central dendrimeric part and the terminal alkyl chains of the carboxylic acids are flexible and are separated by a region with a high density of the ionic ammonium carboxylates (Fig. 11).

Oriented fibres or films of these compounds can be easily obtained, making them interesting as anisotropic ionic conductive materials.

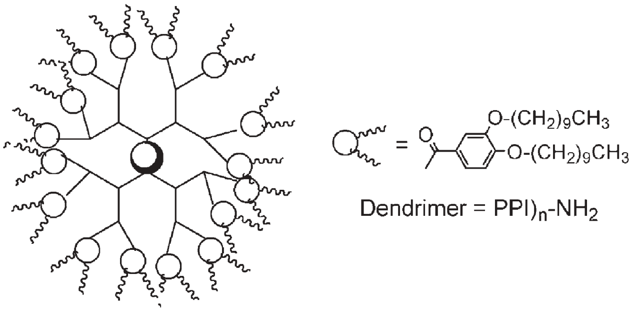

Fig. 10 Poly(propylene imine) dendromesogens substituted with 3,4-didecyloxybenzoyl groups.

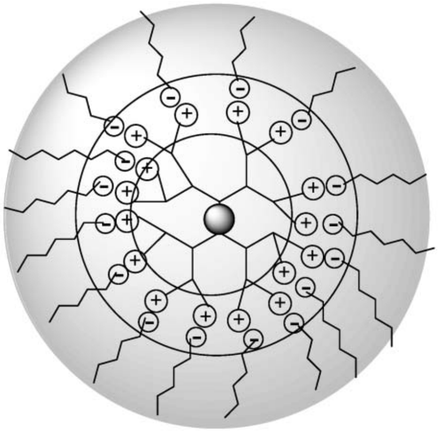

Fig. 11 Schematic representation of the ionic dendrimers.

2.2 Main-chain LC dendrimers

The number of publications dedicated to this class of LC dendrimers is well below that dedicated to side-chain LC dendrimers. This is probably caused by the inherent difficulties in the synthesis of these materials. To date in nearly all the cases, long flexible chains have been introduced in the repeating unit to enhance their solubility and processability. In general, the difficulties in the synthesis have meant that just a few repeating units are introduced in the structure and only the lowest generation dendrimers are synthesized. As for the side-chain LC dendrimers, the mesogenic units condition the kind of mesophase, which in general possesses a higher thermal stability than that of the monomers. This is also observed for the MCLCP (main-chain LC polymers). Representative examples of this group have been reported by Percec *et al.*, where the calamitic units within the skeleton of the hyperbranched polymer promote the formation of nematic, tilted smectic and crystalline phases.[15]

Finally, it is important to review the work by Guillon *et al.*, who have reported main-chain LC homo- and codendrimers.[16] In this last case, they have combined tolane-based and stilbene-based promesogenic units in the same molecule. In the first generation, four units from the former or from the latter unit were introduced. Subsequently, eight units from the alternative promesogenic unit were grafted for the second generation. In this way two different second-generation dendrimers were obtained, called by the authors 'liquid crystalline octopus dendrimers'. As with the SCLC dendrimers, the codendrimers bearing only one terminal chain per branch exhibit lamellar phases, whereas when they bear two terminal chains they exhibit columnar phases, to which the authors have attributed an onion-like structure within the columns.

The most extreme examples of MCLC dendrimers are the so-called intrinsic LC dendrimers, where the dendrimer itself constitutes a discotic supermolecule (Fig. 12). In this case, only the first two generations present a planar geometry, which is not possible for the third generation due to steric reasons. The non-planar conformation entails a lower stability of the liquid crystal behaviour, or even its disappearance.[17,18]

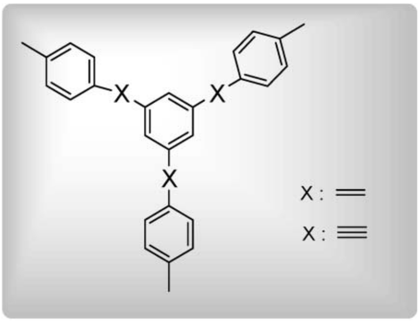

Fig. 12 Intrinsic LC dendrimers reported by Pesak *et al.*[17] (X: triple bond) and Meier *et al.*[18] (X: double bond).

3 Liquid crystal dendrons

As already mentioned in the introduction, dendrons are intermediates in the convergent synthesis of dendrimers. However, their self-assembly behaviour has been intensively studied, and mesomorphism has been reported for a large number of them.

Dendrons are usually represented as "pie-shaped" units with functionalities generally localized on one or both parts A and B (see Fig. 13).

Part A corresponds to the focal point, and it is in general monofunctional. Part B is in contrast a multivalent site.

Many of the phenomena previously observed for LC dendrimers, *i.e.* microsegregation and enthalpy–entropy competition, are also true for dendrons, especially for the highest generation numbers. Thus, a number of examples of main-chain and side-chain LC dendrons have been reported depending on the location of the promesogenic units within the structure of the molecule.

The group of Percec is by far the most active in this area and has shown remarkable control over the structure of mesophases shown by changes in molecular structure. In fact this group has developed a complete library of dendrons of different generations using 3,4,5-trihydroxybenzyl alcohol (3,4,5-AB_3 building block) and 3,4- or 3,5-dihydroxybenzyl alcohol (3,4-AB_2 and 3,5-AB_2 building blocks) as branching units.[19] The dendrons are usually functionalized at the focal point as methyl esters, but other polar groups are also possible. The periphery of the dendron is most often decorated with long aliphatic chains. The LC behaviour of these materials is a consequence of the microsegregation between the soft aliphatic chains, the hard dendritic part and, when applicable, the polar focal point. Therefore the mesomorphism can be tuned by changing the generation number, the branching multiplicity, or the number of terminal alkyl chains. For example, when the 3,4,5-AB_3 building block is used an isomorphous cubic phase

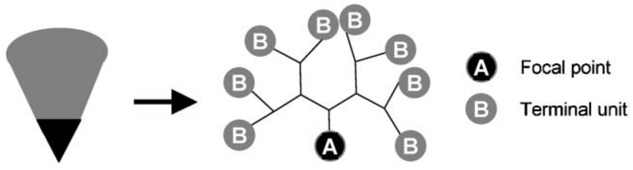

Fig. 13 Schematic representation of a dendron.

is observed with the exception of the first generation, which exhibits a crystalline phase. In the cubic phase, the number of dendrons needed to complete a sphere decreases with increasing generation number.

When the branching multiplicity decreases, the substitution pattern of the branching unit plays a key role (Fig. 14). Thus, a dendron built out of 3,4-AB_2 units favours cubic phases, whereas a dendron of the same generation constructed with 3,5-AB_2 branching units favours columnar phases. The cubic phase of the former is formed in the same way as before for 3,4,5-AB_3 but now a larger number of dendrons is required to complete a sphere. The columnar phase of the latter arises from the dendron adopting the shape of a fragment of disk, which can then self-assemble with other dendrons to form first complete disks then cylindrical structures that may be packed hexagonally. However, at higher generations the alkyl chains cannot be accommodated in a cylindrical surface, and spherical structures are formed rendering cubic phases.[19]

The chemical nature of the chains at the periphery also influences the resulting structure. Replacing the fully hydrogenated terminal chains with homologous fluorinated chains leads to the transformation of the spherical supramolecular dendrimer into a pyramidal columnar supramolecular dendrimer mediated by the fluorophobic effect.[19]

3.1 Combined LC dendrons–active moieties

Some of the most interesting results with LC dendrons are obtained when a functional moiety is incorporated at the focal point (Fig. 15).

In general, the dendritic part of the molecule favours the mesomorphism by including promesogenic units within its structure or long alkyl chains at the periphery. Very often, the dendrons described above are used. A variety of active fragments can be attached at the focal point, delivering the desired property to the supermolecule.

The group of Percec has provided some of the most representative examples in this class as well. For instance, the benzo-15-crown-5 group was attached at the focal point of some so-called Percec-like dendrons and the self-assembling properties of the products were studied. The so-obtained dendrons exhibit liquid crystalline behaviour, whose stability is modified upon complexation of Na^+ ions.[20] When electron-donor or -acceptor organic groups are placed at the focal point of the appropriate dendrons, the π-stacking of the active groups is induced in the centre of a supramolecular helical pyramidal column, yielding materials with high charge carrier mobilities (Fig. 15). These materials could have interesting electronic and optoelectronic applications.[21]

Stupp *et al.* have described macromolecules with rod–dendron and dendron–rod–dendron architectures, formed by biphenyl ester rigid segments and one or two Percec-type polyether dendrons of different generations (3,4,5-AB_3 as building block).[22] Depending on the size of the rod segment and the generation number of the dendrons, these molecules organize in smectic, columnar or cubic phases, with the anisotropic rod–rod interactions being dominant in determining the symmetry of the phase.

Takaguchi *et al.* have described anthracenes bearing a poly(amidoamine) dendritic substituent (anthryl dendrons) which can exhibit mesomorphism (Fig. 15). In the liquid crystalline phase (S_E), the photodimerization reaction of the anthracene moiety proceeds quantitatively and regioselectively to afford only anti-photodimer.[23]

Deschenaux *et al.* have carried out interesting studies on fullerene-containing thermotropic liquid crystals, whose properties could be of interest in nanotechnology (*e.g.* molecular switches, solar cells).[24] They have designed dendritic liquid crystalline fulleropyrrolidines (Fig. 15) which represent an interesting family of electroactive macromolecules, since they combine the electrochemical behaviour of C_{60} with the rich mesomorphism of dendrimers.

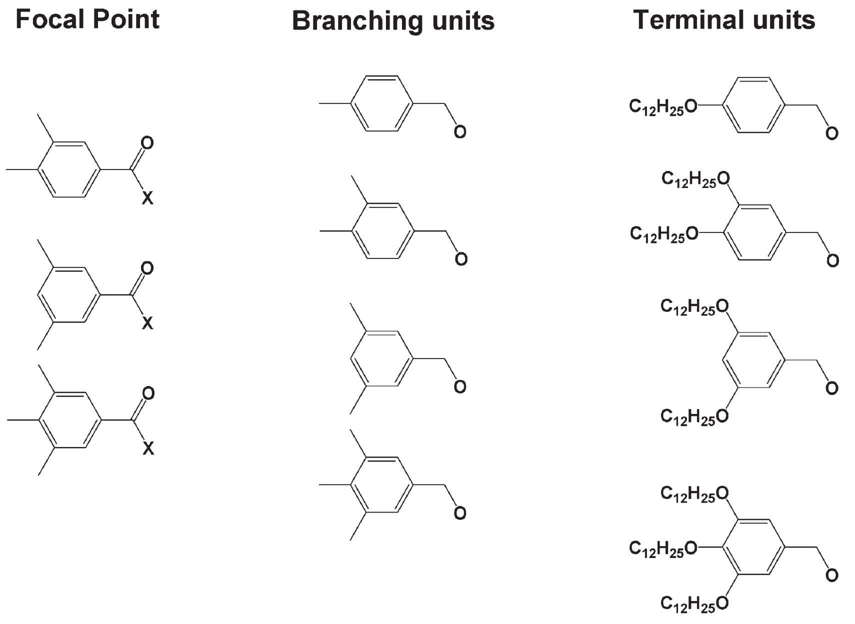

Fig. 14 Different parts combined by Percec *et al.* in their library of dendrons.

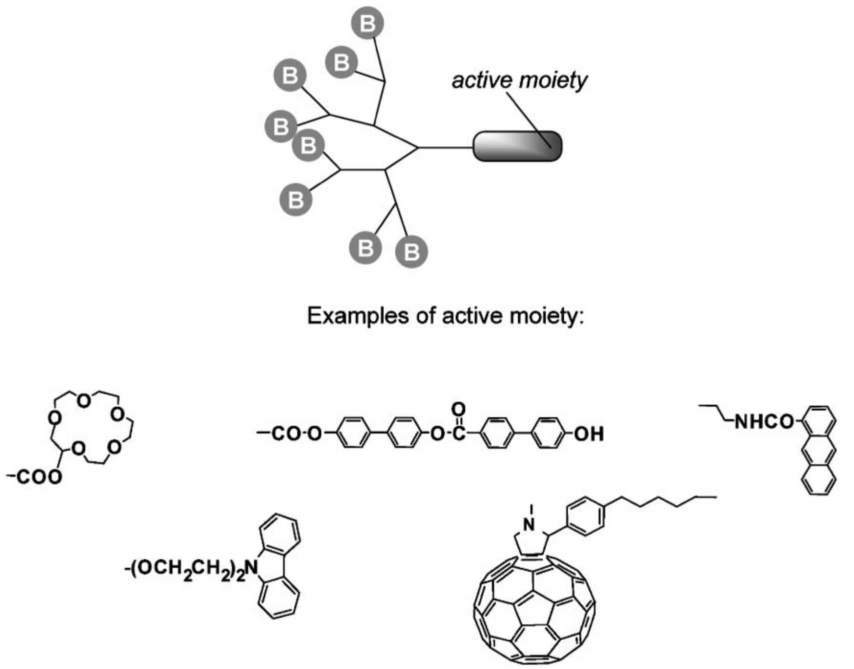

Fig. 15 Structure of mesogenic dendrons bearing an active group.

Depending on the number, the nature and the generation of the dendrons different lamellar organizations are obtained. In general, the fullerene moieties with the dendrimeric part are located between the smectic layers of the promesogenic units. Different substituents can be attached at the N-atom of the fulleropyrrolidine, *i.e.* oligo(*p*-phenylenevinylene)s, ferrocene units, providing suitable candidates for photovoltaic applications or supramolecular switches.

Also of great interest are some amphiphilic dendritic linear block copolymers. These hybrid materials are formed by three blocks, the central one being a poly(ether) aliphatic dendron which bears long linear alkyl chains ($–C_{22}H_{45}$) at the periphery and a 62 repeat units-long linear poly(ethyleneglycol) at the focal point (Fig. 16). This type of compound can exhibit liquid crystalline behaviour owing to phase separation of the polar and apolar segments.[25]

A very interesting possibility related to LC dendrons arises from coupling two different dendrons. Goodby coined for these structures the term ''Janus'' dendrimers (Fig. 17) from Greek mythology although some examples were previously reported which could also fit in the group.[26] The simplest model corresponds to diblock codendrimers formed by two dendrons with different properties or functional groups.

This type of dendrimers opens up numerous possibilities for obtaining multifunctional structures, in which at least one of the sides of the molecule promotes LC behaviour and thus can organize the functionalities present on the other side.

One example is the association of a ferrocene-containing dendron and a dendritic LC structure through a fulleropyrrolidine moiety in the core (Fig. 18).[27]

The ferrocene and the fullerene groups constitute a well-known redox system that displays remarkable electrochemical properties, whereas the liquid crystal dendron induces the formation of SmA phases. The fulleropyrrolidine can be considered the core of a ''Janus'' dendrimer synthesized in a convergent way from the different dendrons. The supramolecular organization promoted by the mesogenic units enhances the photophysical and electrochemical properties of the supermolecule.

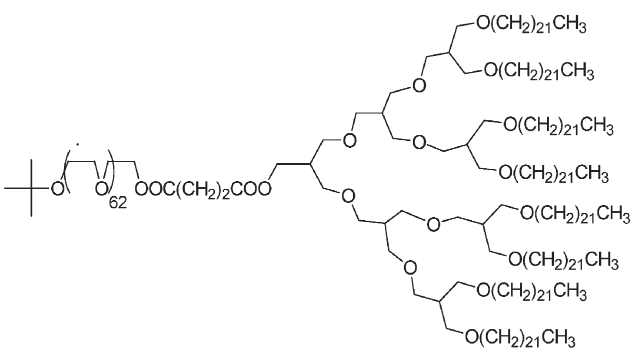

Fig. 16 Molecular architecture of extended amphiphilic dendrimer.[25]

4 Dendronized polymers

Dendronized polymers may be defined in the simplest way as polymers with dendritic side chains; this means that a polymer is used as a polyfunctional, polydisperse core, in which each repeating unit is decorated with a dendron. The research on dendronized polymers is fairly new and the first examples were

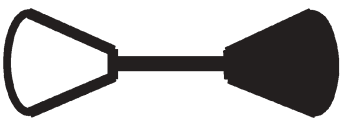

Fig. 17 Janus supermolecular architectures.

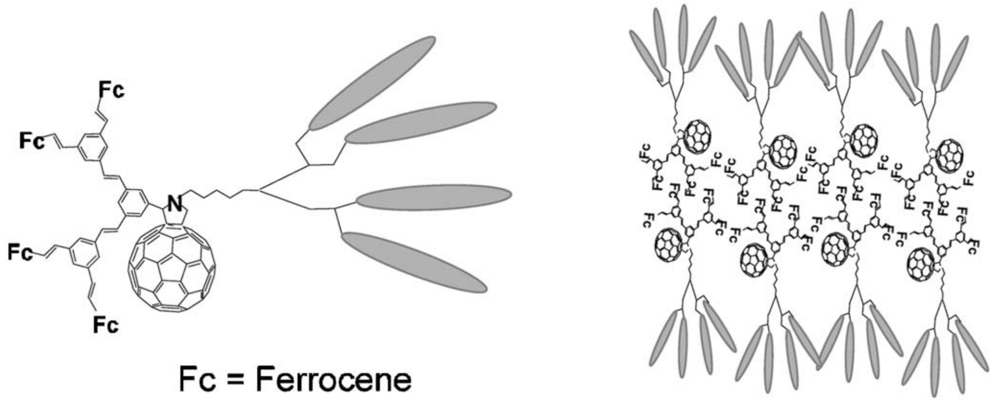

Fig. 18 Liquid crystal fullerene–ferrocene dyads and one proposed supramolecular organization in the mesophase.[27]

reported in a patent filed by Tomalia *et al.* at Dow in 1987. The results of this patent were published in greater detail in 1998.[28] Fréchet and Hawker envisaged that the combination of dendrimers and linear polymers might afford materials with interesting molecular architectures, and in this way, they attached Fréchet type dendrons to a styrene derivative and copolymerized it with styrene in 1992.[29]

Dendronized polymers may be prepared *via* three different strategies from a conceptual point of view: the graft-to, the graft-from and the macromonomer approaches (Fig. 19).

– Graft-to route: A preformed polymer is functionalized with preformed dendrons of the desired generation. It is also called the ‘‘convergent route’’.

– Graft-from route: Dendrons of the first generation are attached to a preformed polymer, and the further generations are prepared by successive reaction with dendrons of the first generation. This strategy is also called the ‘‘divergent route’’.

– Macromonomer route: Dendrons of the desired generation and functionalized with a polymerizable group are polymerized.

There is a large variety of polymer backbones that can be used in the preparation of dendronized polymers: poly(styrene) (PS), poly(methacrylate) (PMA), and poly(*p*-phenylene) (PPP) are often employed. The most common dendrimers – dendrons introduced in dendronized polymers are the so-called Fréchet-type dendrons **1**, poly(amidoamine) (PAMAM) dendrimers **2**, Percec-type dendrons **3**, and Müllen-type dendrons **4** (Fig. 20).

One of the most important of the factors which define the shape of a polymer in the bulk and in solution is certainly the average length of its backbone. On the submolecular level, a

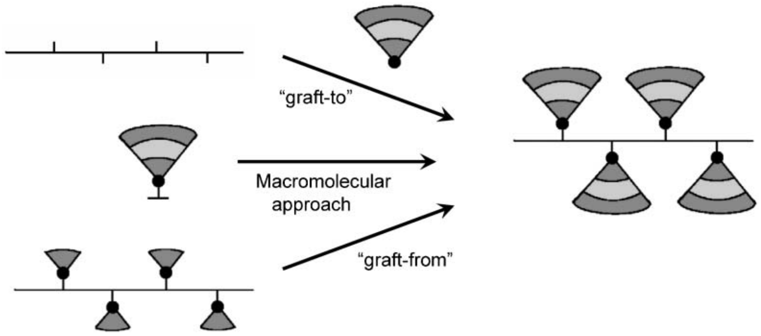

Fig. 19 Schematic illustration of the three synthetic strategies for dendronized polymers.

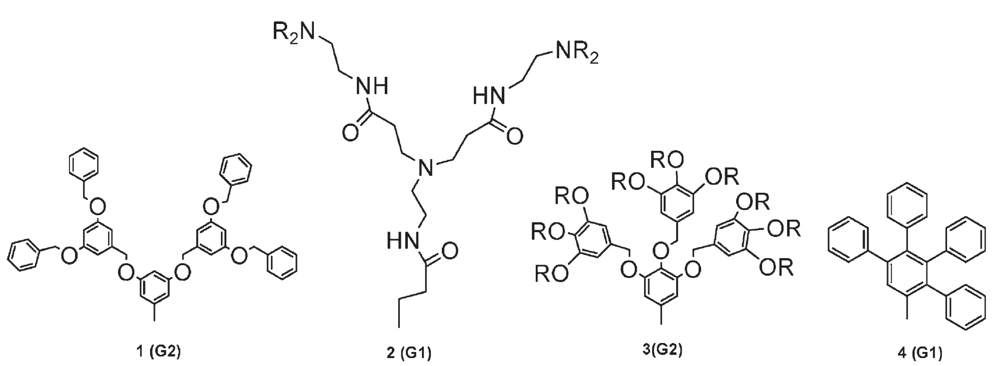

Fig. 20 Structures and schematic representations of Fréchet-type (**1**), PAMAM (**2**), Percec-type (**3**), and Müllen-type (**4**) dendrons.

polymer may be considered as a one-dimensional object, and therefore this may provide potential for anisotropy on the molecular level. However, the overall shape of a polymer depends on the conformations that the backbone may adopt as well. In this sense, only if the polymer is conformationally restricted will an anisotropic shape be the result. Otherwise, the preferred conformation will consist of a random coil with the result of a globular isotropic object. In the case of dendronized polymers, the dendrons around the polymer backbone clearly determine the shape of the polymer because of a number of factors that influence their conformational behaviour:

– The steric congestion induced by the dendrons which is, in fact, a repulsive force.

– The secondary interactions between the dendrons, such as hydrogen-bonding or π–π stacking, which are attractive forces and also favour self-assembly phenomena.

– The microphase segregation of incompatible segments, such as backbone, spacers, dendritic branches, and the periphery, also favours the occurrence of self-assembly processes.

Therefore, the attachment of dendrons of increasing size (generation) to a polymer may be expected to affect the conformational behaviour of the backbone to a marked extent. In fact, it has been shown that a dense attachment of sufficiently high generation dendrons to a polymer converts this linear entity into a cylindrical, rigid and shape-persistent molecular object of nanoscopic dimensions.[30]

In conclusion, high molecular weight, high-generation dendronized polymers are shape persistent, rigid, cylindrical molecular objects with a length that is close to the contour length of the polymer backbone (several hundred nanometres, in some cases), and with an almost monodisperse diameter.

Because of the structural features revealed previously, most dendronized polymers are able to self-assemble into liquid crystal phases. A selection of the work on liquid crystal dendronized polymers is presented now.

The first dendronized poly(methacrylate) displaying liquid crystal properties was reported by Percec and co-workers.[19] The polymer was prepared by a free radical polymerization of the corresponding dendronized monomer. After this first work, the authors investigated the polymerization of related acrylic, methacrylic and styrenic monomers (Fig. 21). The dendronized polymers bearing dendrons of the first generation were shown to exhibit hexagonal columnar LC phases.

The authors proposed a model for the bulk material in which a cylindrical object is formed, with a single polymer chain penetrating its centre. The inner part of the cylinder is occupied by the hydrophilic spacer and the wedge-shaped aromatic dendrons with the alkyl substituents are pointing outward. As explained above, the driving force for this self-organization is both the microphase segregation of incompatible segments of the side chains, and the π–π stacking of the aromatic moieties. As a consequence of the self-ordering of the dendritic side groups, the polymer conformation or shape can be controlled. For example, when attached to short flexible backbones, the dendrons can produce a spherical polymer conformation, whilst when attached to long polymer chains, the self-ordering pattern of the monodendrons gives rise to a cylindrical system.[31] The structure of the dendritic groups plays a role in controlling the conformation and stiffness of the polymer backbone. The ability to control the conformation of polymeric molecular systems using this type of approach is of considerable current interest, with designed folding systems being referred to as foldamers.[32] Such systems mimic the way that proteins fold themselves into well-defined secondary and tertiary structures as a consequence of directed interactions. Percec *et al.* have also utilised hydrogen-bonding dendritic groups as polymer side chains in order to control polymer architecture, with the resultant systems being capable of hierarchical self-ordering to generate LC phases.[19]

Kallitsis and Pakula[33] reported on the synthesis, structure and properties of some dendronized rigid-flexible polyethers prepared by the convergent "macromonomer" synthetic approach. The polymers bear terphenyl main-chain units, carrying two side dendrons in their middle phenylene ring, connected through aliphatic spacers of various lengths.

Recently, Tian and Iyoda[34] have reported on the synthesis, liquid crystalline properties and supramolecular nanostructures of a series of dendronized poly(isocyanide)s. It is well known that poly(isocyanide)s are quite different from conventional polymers such as polystyrene or poly(methacrylate), because of their ability to keep a rigid helical conformation with a pitch of about 0.4 nm even in the racemic polymers. The introduction of liquid crystalline properties into the rigid helical π-conjugated poly(isocyanide)s may render a new class of functional materials with interesting optical and thermal properties.

Mezzenga and Schlüter[35] reported for the first time the use of cationic dendronized polymers and anionic lipids as a model

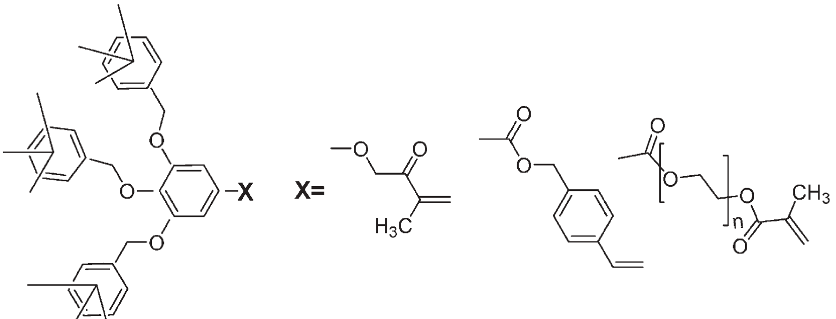

Fig. 21 Examples of dendronized monomers (styrenes, acrylates and methacrylates) used in free radical polymerizations by Percec *et al.*

system to obtain LC properties, in which the molecular architecture can be rationally controlled by two factors, the generation of the dendrons attached to the polymer backbone and the length of the lipid tail.

The polymer of the first generation shows a lamellar phase that can be explained by the segregation of two different domains: the dendronized polymer and the lipid tails. For the polymer of the second generation a tetragonal columnar mesophase is observed. The authors propose the corresponding models for the supramolecular organization which explain the mesomorphic behaviour found.

Because of the reversible nature of the ionic complexation, these results suggest the use of such materials for nanoporous channels, biomimetic, transport and nanotemplating applications.

5 Hyperbranched liquid crystal polymers

Hyperbranched polymers were first reported by Kricheldorf *et al.* in 1982.[36] In contrast to dendrons and dendrimers, hyperbranched polymers can be prepared by a one-step self-polymerization of ABx type multifunctional monomers. The ease of their synthesis and the consequent relatively low price make them the perfect substitutes for dendrimers for applications in which a regular known structure is not a requirement, mainly in materials science. In 1992[37] the first example was reported of a dendritic liquid crystal polymer, which in fact is a hyperbranched nematic liquid crystal polymer (HbLCP). After some years of research focused on LC dendrimers, in the last few years there has been an increase in the research effort directed towards obtaining these hyperbranched liquid crystalline polymers.

As LC dendrimers, HbLCPs can be classified in two groups, namely, main-chain (a) and side-chain (b) hyperbranched LC polymers. In the former group the mesogenic units are introduced during the polymerization as the branching units, whereas in the latter, the mesogenic units may be introduced as terminating groups in the polymerization step but may also be grafted onto a preformed hyperbranched polymer.

The first HbLCPs reported correspond to structures of type (a). In 1994 Percec *et al.*[38] initiated a programme to design dendrimers and hyperbranched polymers which exhibit order in one or more than one dimension in the melt phase. They called these structures "willow-like" dendrimers. The behaviour is explained by taking into account the flexibility of the spacer between the mesogenic units. The branches adopt a *gauge* conformation and allow the mesogenic units to align almost parallel to each other in order to minimize the free volume occupied by the tree (Fig. 22).

Ringsdorf's group[39] synthesized hyperbranched polymers containing chiral terminal groups. These materials show smectic A and cholesteric mesophases in a range from 60 to 150 °C.

Frey *et al.* have developed a synthetic strategy based on the ring-opening multibranching polymerization of glycidol (2,3-epoxy-1-propanol), leading to hyperbranched polyglycerols (tree polymers) with narrow polydispersity.[40] These branched polymers are highly flexible aliphatic polyether polyols to which mesogenic end groups can be attached in order to prepare HbLCPs of structure type (b) (Fig. 23).

In general, all polyglycerols functionalized with mesogenic end groups showed similar phase behaviour. The X-ray diffraction patterns and the optical microscopy observations unambiguously proved the presence of a nematic phase of low viscosity, in contrast to the smectic behaviour of the structurally related dendrimers with mesogenic end groups. Specific properties of branched molecules, such as the absence of entanglements and the high concentration of end groups, are promising for the preparation of LC materials with lower viscosity than linear polymers and possibly shorter switching times.

In all HbLCPs described until now, the mesogenic groups are attached covalently at the surface groups of the hyperbranched liquid crystal polymers. In recent years polymer–amphiphile complexes based on specific non-covalent interactions, such as hydrogen bonding, charge transfer, ionic interactions or coordination complexation, have received considerable attention due to their simple fabrication, interesting properties and potential applications.

Very recently, in 2005 Tsiourvas *et al.* reported the preparation of supramolecular LC materials exhibiting smectic A phases, based on the complexation of pyridinylated hyperbranched polyglycerol and cholesterol-based carboxylic acids *via* hydrogen bonding.[41]

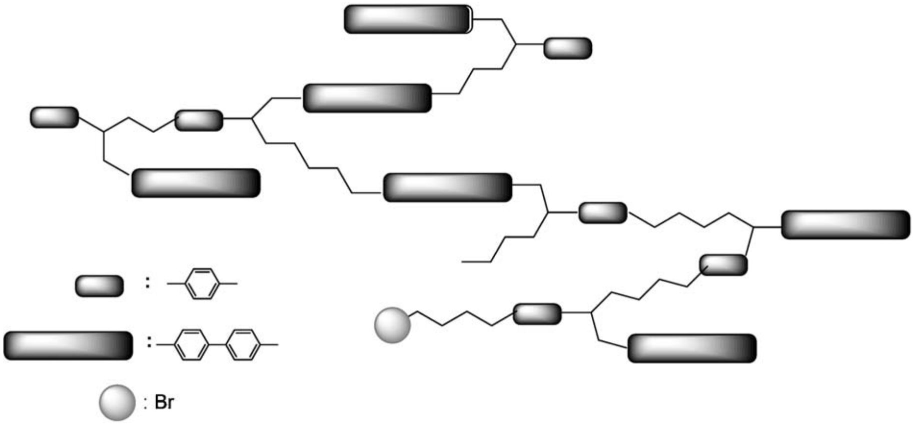

Fig. 22 Willow-like dendrimer in the nematic state.

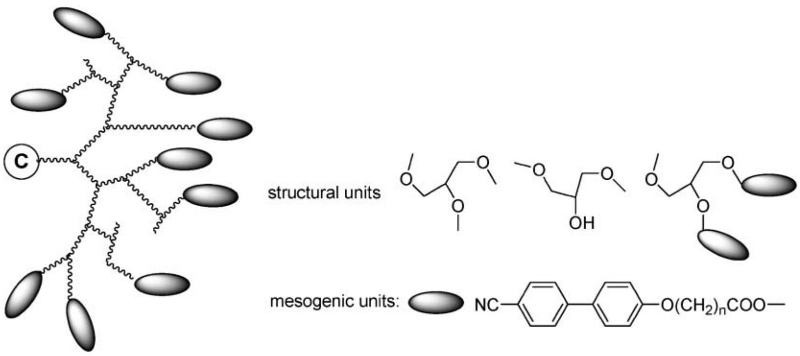

Fig. 23 Schematic representation of hyperbranched polyglycerol with mesogenic units.

Commercially available hyperbranched poly(ethylene imine)s (PEIs) have been complexed with fatty acids by several authors.[42–44] All the complexes described exhibit lamellar mesophases in analogy to the analogous ionic LC dendrimers.[14] However, the viscosity of the resulting smectic A phase makes these complexes useless for application.

One strategy to avoid this problem is to look for supramolecular HbLCP displaying the less viscous nematic mesophase. In this way, Frey *et al.* have reported, at the same time, the formation of nematic mesophases in supramolecular complexes prepared from the non-covalent interaction of methylated hyperbranched PEI (PEIMe)s with a mesogenic carboxylic acid, namely, 5-(*p*-cyanobiphenoxy)pentanoic acid (CBPA) (see Fig. 24). This is the first nematic ionic HbLCP described to date.[45]

Conclusions

Liquid crystal dendrimers present some intrinsic features that make them different to the conventional structures of other mesogenic materials. It is well known that the mesogenic behaviour is clearly determined by very weak intermolecular interactions. Due to the freedom of molecular movement which is inherent to the liquid crystal state, molecules are located in the most appropriate positions so that these interactions are maximised. Microsegregation also plays a key role in some cases, and the liquid crystal order is accomplished by the presence of nanodomains with different molecular orientations in regular positions.

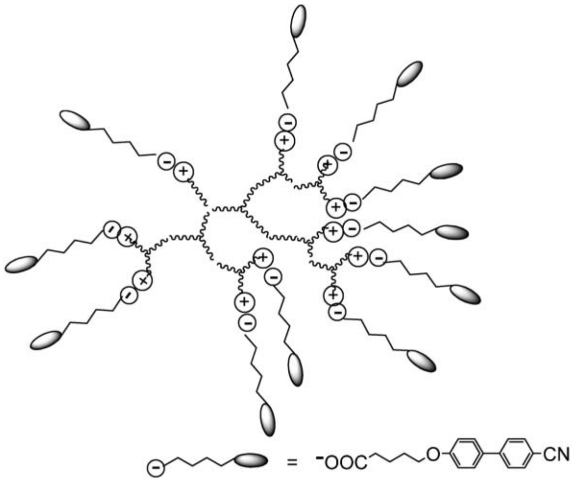

Fig. 24 Schematic representation of methylated hyperbranched PEI (PEIMe)s with a mesogenic carboxylic acid (CBPA).

In the case of dendrimers and other dendronized structures, the promesogenic units are arranged in a highly congested environment, and their mobility is therefore restricted. In such hypercongested structures, the decrease of the freedom of movement and the microsegregation phenomenon lead to molecular geometries and properties that are not achievable with other conventional liquid crystal systems.

Moreover, the microsegregation phenomenon may be used either favouring or disfavouring the occurrence of a liquid crystal phase, which results in an increase of the versatility of LC dendrimers. In fact, these materials are an excellent tool to progress in the knowledge of the structure–activity relationship in liquid crystals.

The structural and synthetic versatility of LC dendrimers allows the design and preparation of different types of molecular arrangements by use of the most appropriate dendrimeric part in each case. To this singular property of these materials, some others can be added by the introduction of active moieties, giving rise to a wide variety of functional materials. It shouldn't be forgotten that for each structure type presented here, different functionalities could be introduced in different parts of the molecule. Thus, with an adequate design and selection of properties extraordinary materials can be obtained, which otherwise would be accomplished only with great difficulty. Some of the materials reviewed here make use of these possibilities, which are still just a few with respect to the numerous potential applications that will appear in the near future.

Acknowledgements

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