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Non-conventional liquid crystals—the importance of micro-segregation for self-organisation

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Selected examples of recently synthesised non-conventional liquid crystals are highlighted. These are cyclic and open chain oligoamides, molecules containing tetrahedral or octahedral central cores, dendrimers, polyhydroxy amphiphiles, taper shaped molecules, liquid crystals with perfluorinated or oligosiloxane segments, rod-coil molecules as well as special types of polycatenar and laterally branched calamitic molecules. Their mesomorphic properties are discussed as a consequence of incompatibility, micro-segregation and space filling. The analysis is based on the general concept of amphiphilicity, which describes any chemical or structural contrast within a molecule, such as hydrophilic/lipophilic, polar/non-polar, hydrocarbon/fluorocarbon, oligosiloxane/hydrocarbon or rigid/flexible. These non-conventional liquid crystals will be regarded as block molecules. Depending on the degree of chemical and structural difference and the size of the different building blocks micro-segregation can occur with formation of lamellar, columnar or spheroidal aggregates which organise to smectic, columnar and cubic mesophases. The striking analogies between the polymorphism of thermotropic and lyotropic liquid crystals and block-copolymers are pointed out.

Introduction

The transition from the highly ordered crystalline solid to the disordered isotropic liquid state often occurs in a multistep process *via* intermediate phases (mesophases) which are designated as liquid crystalline phases.[1] In these phases the order of the crystalline state is only partly lost and the individual molecules have already got some degree of mobility. These mesophases can occur in pure materials with dependence on the temperature[2] (thermotropic mesophases) as well as in multicomponent systems with dependence on their composition and the temperature (*e.g.* lyotropic phases). Because liquid crystals combine order and mobility on a molecular level they are important in materials science as well in the life sciences. Important applications[3] of thermotropic liquid crystals are electrooptical displays, temperature sensors and selective reflecting pigments.[4] Lyotropic systems are incorporated in cleaning processes[5] and are important in the cosmetics industry, they are used as templates for the preparation of mesoporous materials[6] and serve as model systems for biomembranes.[7] Furthermore the liquid crystalline state is ubiquitous in living matter. Most important are the biological membranes, DNA can form lyotropic mesophases[8] and natural silk is spun by the silkworm *Bombyx mori* from an aqueous nematic liquid crystalline phase of fibroin.[9]

1.1 Low molecular weight liquid crystals

The examples mentioned above indicate that liquid crystals can have quite different molecular structures. In a classical approach, substances that can produce liquid crystalline phases are considered to belong to one of two distinct classes of materials: the nonamphiphilic but anisometric mesogens and the amphiphilic molecules. The first class includes anisometric, rod- or disc-like molecules or aggregates in most cases giving exclusively thermotropic liquid crystals. The second class includes amphiphilic molecules such as detergents and lipids leading to lyotropic,[10] and also thermotropic mesophases.[11] Both types of mesogenic molecules can be attached to a polymer backbone (LC-side-chain polymers) or they can be incorporated in the polymer backbone (LC-main-chain polymers).[12] More recently the interest in thermotropic and/or lyotropic mesophases of rod-like polymers (hairy rods, polypeptides, polyisocyanates, cellulose derivatives *etc.*)[11a] has grown. Typical examples of the main types of molecules forming liquid crystalline phases are shown in Fig. 1. Additionally, the different molecular structures have been combined. Polycatenar[13] compounds for example have a structure intermediate between rod-like and disc-like molecules and amphiphilic molecules have been combined with anisometric structural units to bridge the gap between thermotropic and lyotropic liquid crystals.[11a]

Regardless of the molecular structure, liquid crystalline phases can be classified according to the degree of long range order of their constituent parts and the symmetry within the mesophases.[1] An overview of the main phase types is given in Figs. 2–4.

Mesophases in which the positional long range order is maintained, but orientational order is lost are termed disordered crystals or plastic crystals.[14] If the orientational order

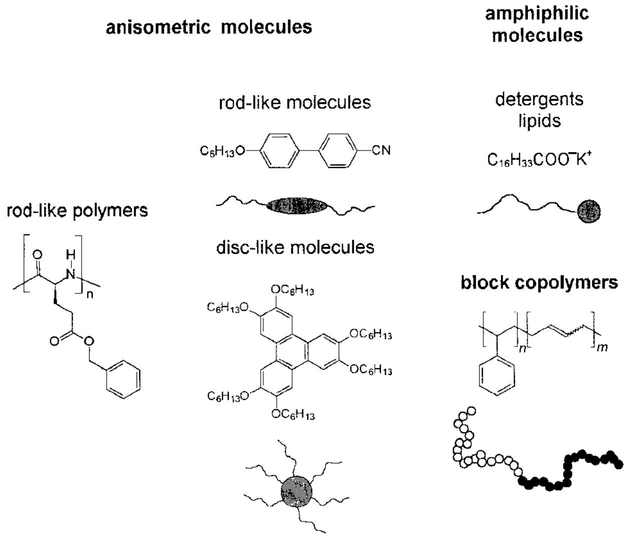

Fig. 1 Typical examples of the main types of molecules forming liquid crystalline phases

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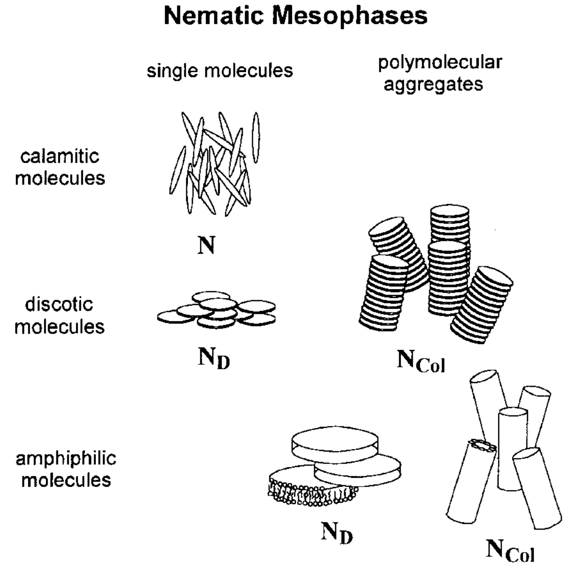


Fig. 2 Schematic representation of the different nematic mesophases formed by the organisation of calamitic molecules (N), disc-like molecules (N_D), columnar aggregates of disc-like molecules (N_{col}) and polymolecular aggregates of amphiphilic molecules (rod-like micelles: N_{col}, plate-like micelles; N_D)

is maintained, but the positional long range order is completely lost the mesophases are termed nematic liquid crystals (Fig. 2). However, the positional order is often only lost in one or two dimensions. These mesophases will be designated as positional ordered mesophases (Fig. 3).

The most important positional ordered mesophases are the smectic (S), the columnar (Col) and the cubic (Cub) phases. Rod-like molecules predominantly form smectic phases. In Fig. 3 only smectic phases of the fused type, *i.e.* without additional positional order in the layers (S_A and S_C), are shown. Some polar calamitic molecules can form mesophases in which the smectic layers are collapsed into ribbons ($S_A{}^{\sim}$ and $S_C{}^{\sim}$).[15] Because the ribbons can be organised in a rectangular or in an oblique 2D-lattice, these mesophases could alternatively be described as columnar phases (Col_r, Col_{ob}). Columnar phases of the ribbon-type, and S_C-phases can also be found for polycatenar molecules,[13] which have a shape intermediate between rod-like and disc-like molecules (for an example see Table 5). In this class of compounds cubic phases (Cub_V) can occur as intermediate phases between layer-like and columnar organisation of these molecules. *Ia3d* and *Im3m* cubic lattices have been found.[16] In Fig. 3 two possible structures of these lattices are shown; the detailed arrangement of the molecules in these cubic lattices however, is not yet clear.

Disc-like molecules preferably organise to columnar mesophases. The L_D-phase, which is seldom observed, represents a layer-like organisation of discotic molecules.[17]

A wide variety of different mesophases is found for amphiphilic molecules in the pure state,[11,18] which is shown in the lower part of Fig. 3. Their mesomorphic properties can be influenced by addition of protic solvents, which results in the formation of lyotropic mesophases (see Fig. 4).[10] In thermotropic and in lyotropic mesophases of these amphiphilic molecules, different types of cubic phases (Cub_V and Cub_I) can also be detected in addition to the smectic and columnar mesophases.[18,19] These cubic phases, which can occur in different classes of compounds, represent a fascinating state of matter, because they are three-dimensionally ordered crystals of fluid polymolecular aggregates. The different types of cubic lattices found in lyotropic systems of amphiphilic molecules are shown in Fig. 4(b). In many cases, however, the structure of the cubic phases is still unclear.

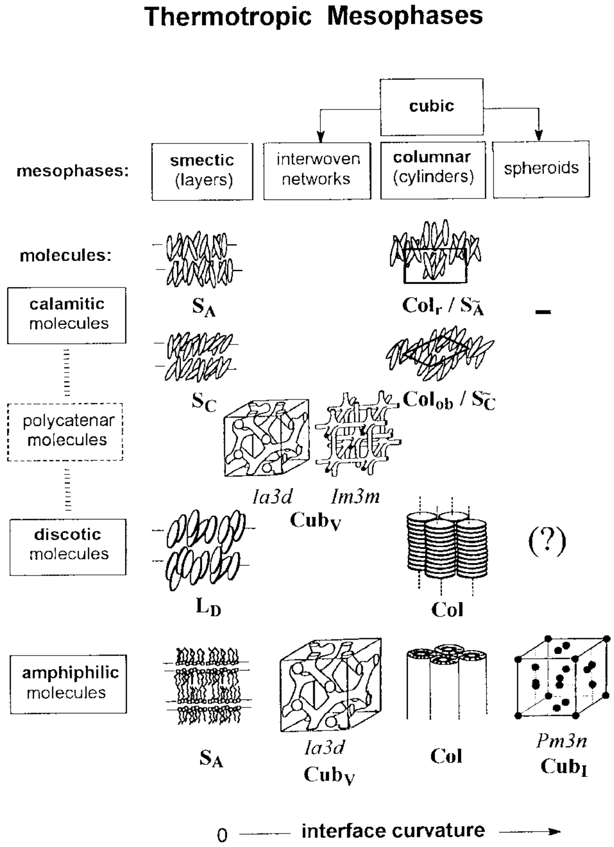


Fig. 3 Positional ordered fluid thermotropic mesophases formed by calamitic, polycatenar, disc-like and amphiphilic molecules. Abbreviations: S_A = smectic A-phase, S_C = smectic C-phase (the lamellar phases are shown as cross sections of a segment of the layers which are extended laterally and in the third dimension), $S_A{}^{\sim}$ = antiphase, $S_C{}^{\sim}$ = ribbon phase [ribbon-like segments of the smectic layer which are extended in the third dimension and arranged in a centred rectangular ($S_A{}^{\sim}$, Col_r) or oblique ($S_C{}^{\sim}$, Col_{ob}) 2D-lattice],[15] L_D = lamellar (smectic) mesophase consisting of disc-like molecules;[17] Col = columnar mesophases, Cub_V = bicontinuous cubic mesophase consisting of mutually interwoven networks of branched cylinders, Cub_I = discontinuous cubic phase consisting of spheroids.[18,77]. Space groups of the cubic phases are given in italics.[19] The arrangement of the molecules in the cubic mesophases of polycatenar compounds is not yet clear. Presumably, they represent mutually interwoven networks of ribbons.[16] The thermotropic mesophases of amphiphilic molecules usually represent inverted phases (type 2).[82] Then, the branched cylinders of the Cub_V-phase represent the head group areas embedded in the lipophilic continuum of the molten alkyl chains. The Cub_I-phases consist of eight nonglobular spheroidal micelles per unit cell,[77,78,90] only their position in the unit cell is shown, an explanation of a model based on prolate micelles is given in Fig. 4(b).

The remarkable feature of amphiphilic molecules is the tendency of their hydrophilic and hydrophobic parts to segregate in space into distinct microdomains. Owing to the chemical bonding of the amphiphatic parts, segregation does not lead to macroscopic phase separation. Instead, it results in the formation of different regions which are separated by interfaces at a molecular scale. These interfaces have characteristic mean interface curvatures, which are largely determined by the mean lateral areas of the competing parts of the amphiphilic molecules.[10,20] Non-curved planar aggregates organise into lamellar (smectic) mesophases. A finite mean interface curvature gives rise to cylindrical aggregates of one component embedded in a continuum of the other component. Extended non-branched columns can organise to columnar mesophases (Col). Branched columns occur at the transition between lamellar and columnar mesophases.[21] They form three-dimensional interwoven networks which can organise into different cubic lattices [bicontinuous cubic mesophases, Cub_V-phases, see lower part of Fig. 4(b)]. Further increasing the interface curva-

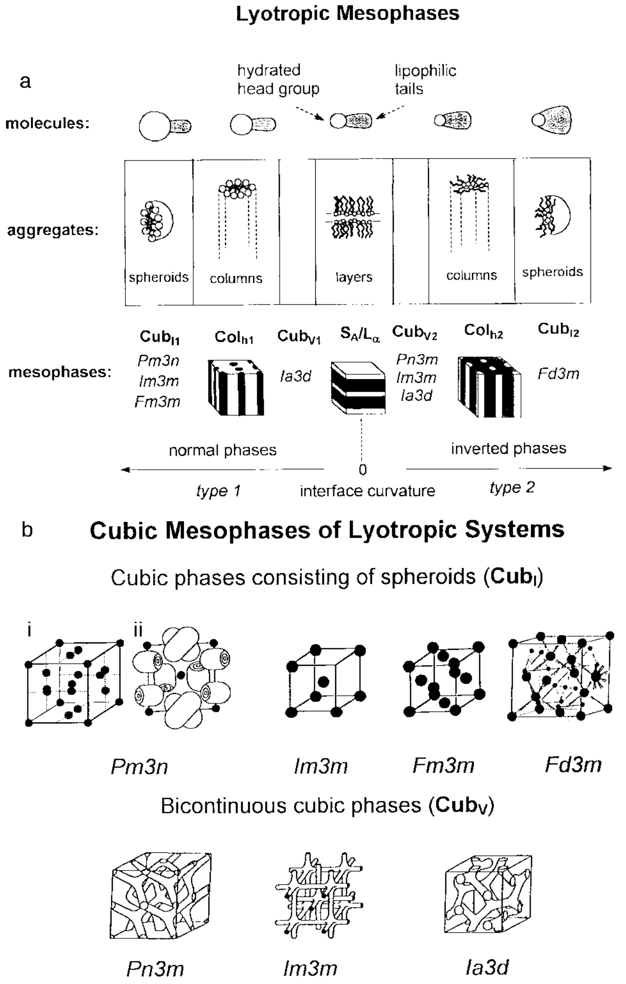


Fig. 4 a: The main lyotropic mesophases that depend on the interface curvature.[10] Abbreviations: L_α = lamellar (smectic A) phase; for the other abbreviations, see Fig. 3. Space groups of the cubic phases found in the different regions of the phase diagram are given in italics.[19] Additional non-cubic phases (*e.g.* tetragonal phases) are possible at the transition from the smectic to the columnar phases.[10,19] b: Cubic lattices occurring in lyotropic systems.[19] Their position in the lyotropic phase sequence is shown in Fig. 4a. The displayed branched cylinders and the spheroids can represent the headgroup areas (plus solvent) embedded in the lipophilic continuum of the molten alkyl chains (inverted phases, type 2). In the normal phases (type 1) the cylinders and micelles represent the regions of the lipophilic chains surrounded by the head-groups embedded in the polar solvent. The Cub_I-phase of the *Pm*3*n*-type consists of eight nonglobular spheroids per unit cell, only the model assuming prolate micelles is shown[19b] [i: arrangement of the micelles in the cubic lattice; ii: view upon a face of the cubic lattice built up by prolate micelles, the micelles in the centre and at the corners are rotationally disordered and are represented by dots; adapted from ref. 19(*b*)].

ture leads to spheroids—closed globular or non-globular micelles—which can also organise into different cubic lattices [discontinuous cubic phases, Cub_I-phases, see upper part of Fig. 4(b)].[18,19]

The interfaces between the segregated regions can be curved away from the regions with stronger cohesive forces (the stronger cohesive forces are found in the continuum surrounding the aggregates, normal phases, type 1) or in the direction of these regions (the stronger cohesive forces are found within the aggregates, inverted phases, type 2).

The microstructure of the different thermotropic and lyotropic liquid crystalline phases can easily be determined by microscopy between crossed polarisers which allows a reliable differentiation between nematic, smectic A, smectic C, smectic low-temperature phases and columnar phases by their typical optical textures. These textures are the result of the birefringence of the liquid crystalline phases and typical defect structures, which are influenced by the molecular organisation. Contrary to all other mesophases, the cubic phases are optically isotropic. They can be distinguished from the isotropic liquid state by their high viscosity and the crystal-like shape with cornered phase boundaries of their domains while growing from other phases [see Fig. 5(b)]. Selected examples of the optical textures of smectic, columnar and cubic mesophases are shown in Fig. 5. More detailed investigation of the molecular organisation (differentiation of low-temperature smectic phases, differentiation between different types of columnar and cubic phases), however, requires X-ray diffraction, NMR methods and further investigations.

1.2 Block-copolymers

In recent decades it was found that block copolymers can also produce well-developed liquid crystalline phases (Fig. 6).[22] In the most simple case AB-diblock copolymers are made up of two chemically distinct blocks, A and B, covalently bonded to form a single chain. Here, mesomorphic properties are caused by the incompatibility of the different polymer blocks.[22] Different polymers are, in general, incompatible. Because of

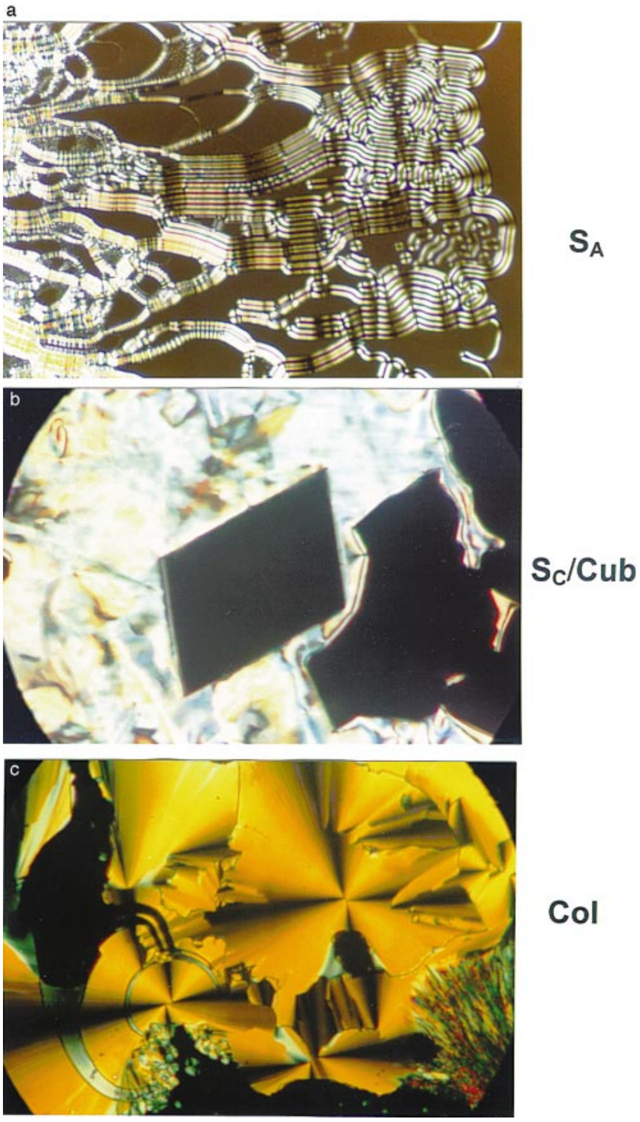


Fig. 5 Selected examples of typical textures of liquid crystalline phases as observed between crossed polarizers. a: Oily streaks texture with Myelin-figures of a lyotropic smectic A-phase. b: Bicontinuous cubic mesophase (black areas) as growing from a smectic C-phase. c: Columnar mesophase.

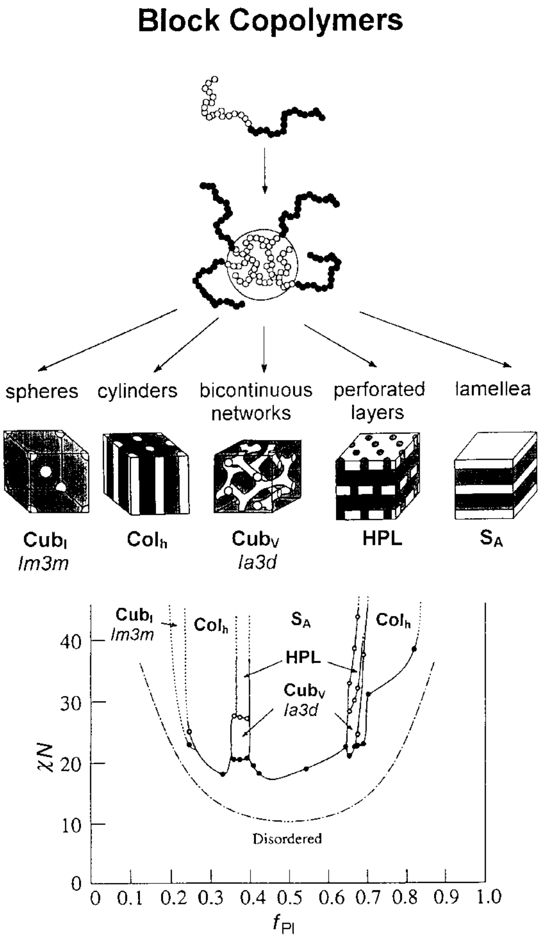


Fig.6 χN *versus* f_{PI} (PI = polyisoprene) phase diagram for poly(isoprene-β-styrene) diblock copolymers (reprinted with permission from ref. 29, copyright American Chemical Society) and morphologies of the ordered structures. Abbreviations: HPL = hexagonal perforated layers; for the other abbreviations, see Fig. 3.

the large size of polymer molecules, the entropy gain on mixing is very small and in the absence of specific favourable interactions between the two polymers, it cannot compensate for the enthalpy loss that occurs. With block copolymers, these incompatibility effects give rise to a segregation of the different polymer blocks into distinct micro domains. However, the fact that the different blocks A and B are chemically connected prevents macroscopic phase separation, leading to microphases with A-rich and B-rich domains separated by internal interfaces. The micro-segregation can be observed below a certain order–disorder temperature, which depends on the size of the blocks and on the degree of chemical and structural difference between the blocks. More precisely the important parameters which govern phase separation for A–B diblock copolymers are the total degree of polymerisation $N = N_A + N_B$, the segment interaction parameter (Flory–Huggins parameter χ_{AB}) and the volume fraction of the components f.[23,24] The segregation between the two blocks is dictated by the product of N and χ_{AB} whereas the interfacial curvature is controlled by f. The Flory–Huggins parameter χ_{AB} can be estimated according to eqn. (1)

$$\chi_{AB} = V_R(\delta_A - \delta_B)^2/RT \qquad (1)$$

where δ_A and δ_B represent the Hildebrand solubility parameter and V_R a reference volume. Thus χ_{AB} which is a measure of the incompatibility between A and B depends on the difference in the intermolecular interactions in the segregated regions (expressed as the different solubility parameters δ_A and δ_B) and on the temperature T. At low $N\chi_{AB}$ (high temperature) a diblock copolymer melt is homogeneous. The order–disorder transition occurs when $N\chi_{AB}$ is increased (low temperature). For symmetric block polymers with $f_A = f_B = 0.5$, the melt is ordered in a lamellar structure (LAM). As one block (B) is made longer at the expense of the other block (A), the morphology changes to columns (molar fraction of the minor block, f_A about 0.3–0.4)[25] and then to spheres ($f_A < 0.3$) of component A embedded in a continuum of the major component B. These morphologies represent equilibrium states with the lowest free energy. Because the interaction energy between the segregated regions is mainly localised at their interfacial region, the systems are in equilibrium only when the total area of the interfaces is a minimum. The domains are regular, often forming columnar and cubic mesophases. Besides these classical phases, additional complex structures, such as hexagonally modulated layers (HML), hexagonally perforated layers (HPL)[26] and cubic (gyroid) phases with the space group *Ia*3D[27] have been found in a narrow range of f and $N\chi$ between lamellar and columnar morphology near the order–disorder transition. Some of these intermediate states may be non-equilibrium states.

Above $f_A = 0.5$ there is an inversion of the role of the two components. Because the blocks are different, especially due to conformational asymmetry,[28] , the $N\chi$ *versus* f diagrams of diblock polymers are not symmetric in respect to $f = 0.5$. As an example the $N\chi_{AB}$ *versus* f diagram for a polyisoprene–polystyrene diblock copolymer is shown in Fig. 6.[29]

The analogy of the mesophases formed by block copolymers with those of amphiphilic molecules is striking and block copolymers can be regarded as polymeric analogues of simple amphiphiles. Like amphiphiles, they can form not only thermotropic phases as pure materials. The addition of selective solvents to one or the other components of the block copolymer can affect the morphology by changing the effective volume fractions of the components. A lamellar phase can be changed *via* a cylindrical to a spherical morphology on addition of a solvent selectively interacting with one of the blocks. If these mixed systems are ordered, they can be regarded as lyotropic mesophases. In a recent example six different mesophases and two micellar solutions (L_1, L_2) have been realised for a poly(oxybutylene)-b-poly(oxyethylene)–water–xylene system:[30]

$$L_1\text{—}Cub_{I1}\text{—}Col_{h1}\text{—}L_\alpha\text{—}Cub_{V2}\text{—}Col_{h2}\text{—}Cub_{I2}\text{—}L_2$$

Thus almost the whole 'hypothetical lyotropic phase diagram' (see Fig. 4) was scanned. Also micelles and organised films at interfaces can be formed by block copolymers.

The analogy of the mesophases of block copolymers with the smectic and columnar ordering of nonamphiphilic liquid crystals and the importance of the amphiphilic character[31] and micro-segregation for mesomorphic self-organisation have been pointed out several years ago.[22a–c] The calamitic mesogens for example can be regarded as block compounds composed of a rigid block terminated by flexible alkyl chains forming predominantly lamellar structures due to the segregation of the incompatible molecular parts.[31] Furthermore, it was proposed that thermotropic and lyotropic mesomorphism can be viewed as the consequence of division of space into two media separated by interfaces, generated by the assemblage of chemical groups with different affinities.[32] Thereby, the curvature of the interfaces is largely determined by the molecular structure: rigid molecules favour the formation of flat interfaces, if they are rod-like and they favour cylindrical ones when they are disc-like. For flexible molecules, the interface can adapt different shapes with dependence on the temperature and solvent concentration.[32]

An early attempt to quantitatively describe micro-segregation in lyotropic systems of amphiphilic molecules was provided by the R-theory of fused micellar phases.[14] Biphilic asymmetry, flexibility asymmetry, electric and steric asymmetry have been introduced to describe thermotropic and lyotropic systems in the framework of a generalised molecular asymmetry model.[33] In recent years several authors have discussed micro-segregation as an additional driving force for columnar mesomorphism in some non-conventional mesogens.[34–39] In this way, it becomes more and more evident that the important structural entity of all positional ordered liquid crystalline phases is not the molecule, but the interface built up by the organisation of the molecules.[32] Thus, the concepts of thermotropic and lyotropic liquid crystals and block copolymers are closely related and it is often only a difference in semantics, like the notation $\mathrm{S_A}$, $\mathrm{L_a}$, G and LAM, that actually denote an ordered array of non-curved (layer-like) aggregates or the notations $\mathrm{H_\alpha}$, $\mathrm{Col_h}$, $\mathrm{D_h}$, Φ_h, $\mathrm{O_h}$, M, HEX, *etc.*, which all denote mesophases consisting of hexagonally ordered columns. In this paper we will use the descriptor S for lamellar (smectic) layer structure, Col[40,41] for columnar mesophases, $\mathrm{Cub_V}$ for bicontinuous cubic mesophases, and $\mathrm{Cub_I}$ for micellar cubic phases,[42] irrespective of whether they occur in thermotropic or lyotropic systems or in the phase sequence of block copolymers.

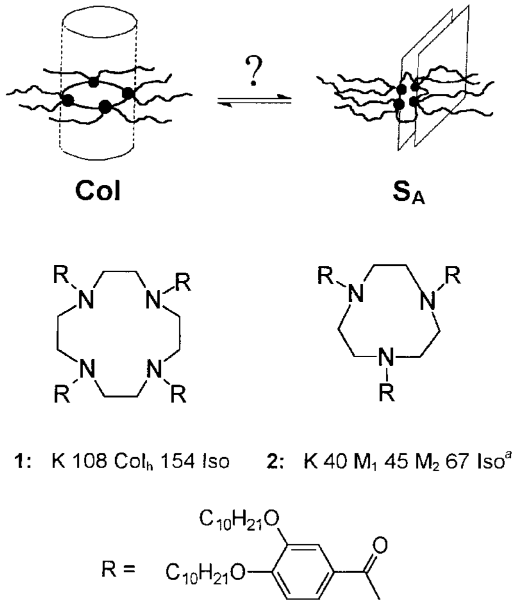
1.3 Scope of this feature article

In this feature article, selected examples of recently synthesised non-conventional mesogens will be highlighted and their mesomorphic properties will be discussed as a consequence of incompatibility, micro-segregation and space filling, pointing out the striking analogies between the polymorphism of block-copolymers, and thermotropic and lyotropic liquid crystals.

We will focus our interest especially on materials that can undergo transitions between different phase morphologies by structural variations and/or on addition of solvents. It seems that mesophases consisting of columnar aggregates are ubiquitous in all types of organised soft matter. Therefore columnar mesomorphism will be systematised and discussed in more detail in a separate feature article.[43] Here we treat columnar mesophases only if their occurrence is mainly caused by micro-segregation.

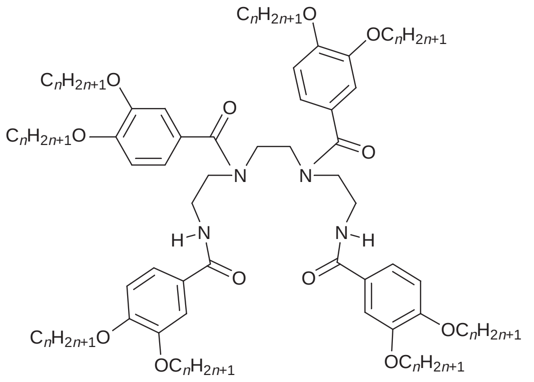
2 Cyclic and open chain oligoamides

Polyacylated azacrowns have been found to exhibit liquid crystalline properties.[44] Two selected examples are shown in Fig. 7. At first, it was thought that the average disc-like shape of these azamacrocycles is responsible for their columnar mesomorphism. However, the rather flexible central core allows different molecular conformations: an elongated one with a rod-like shape and a radial one with disc-like character (see

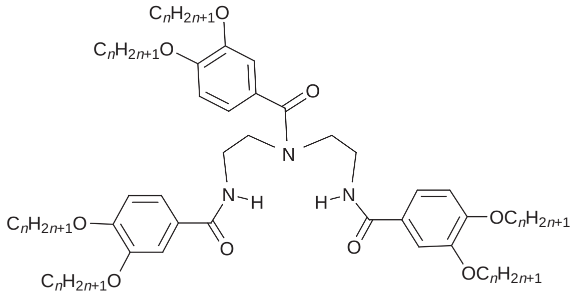


1: K 108 $\mathrm{Col_h}$ 154 Iso **2**: K 40 $\mathrm{M_1}$ 45 $\mathrm{M_2}$ 67 Iso[a]

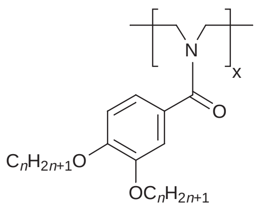
Fig. 7 Phase transition temperatures (*T*/°C) of two selected mesogenic azacrown derivatives **1**[45] and **2**[44b] and schematic sketch of two possible conformations. [a]From X-ray data it was suggested that M represents a lamellar (smectic) mesophase.[41]



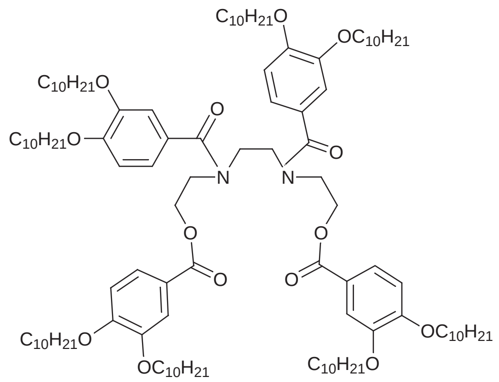
3a $n = 10$ K 93.5 $\mathrm{Col_h}$ 104 Iso[a]
3b $n = 16$ K 116 (Col 84 Cub 104.5) Iso



4a $n = 5$ K 86.3 Cub 104.4 Iso
4b $n = 10$ K 117.5 (M 102.5) Iso[b]
4c $n = 16$ K 85.3 Cub 106.9 Iso



5 $n = 10$ K 61 $\mathrm{Col_h}$ 120 Iso[c]



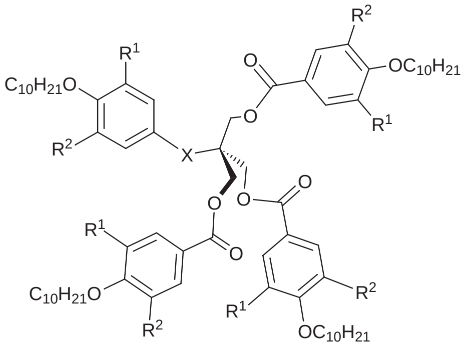
6 g 15 Col 68 Iso

Phase transition temperatures (*T*/°C) of selected open chain oligoamides **3**,[41] **4**,[46] compound **6**,[36,39] and the polyamide **5**.[45] [a]K 99 ($\mathrm{Col_h}$ 93) Iso[45]. [b]From X-ray data it was suggested that M represents a lamellar (smectic) mesophases; however the optical texture is similar to a columnar phase.[46] [c]K 62 $\mathrm{Col_h}$ 103.3 Iso[36].

Fig. 7).[41] Indeed, smectic phases were proposed for some azamacrocycles, such as 1,4,7-triazacyclononanes **2** having 3,4-dialkoxybenzoyl substituents, despite their—at first glance—disc-like molecular shape.[41]

Recently, it also was reported, that the open chain analogues of these cycles also display thermotropic liquid crystalline behaviour.[39,41,45–47] At first it was assumed that the appearance of columnar mesophases in the case of many open chain compounds such as **3** and **4** is caused by the formation of disc-shaped individual molecules by cyclisation *via* hydrogen bonding[45,47] or by formation of polymolecular aggregates with a helical backbone. But later it was found that polyamides such as **5**[36,45,47] and even the ester compound **6**[39] which lack a proton donor and thus lack the ability to form hydrogen bonding as pure materials also display thermotropic mesophases. This shows that the formation of anisometric core structures *via* hydrogen bonding is not necessary for mesophase formation. Furthermore, these compounds do not represent amphiphiles in a classical sense and therefore they do not belong to one of the classical types of liquid crystal forming compounds mentioned above.

Table 1 Thermotropic transition temperatures (T/°C) of selected liquid crystals **7**,[37] **8**[49] and **9**[51] with a tetrahedral central core



Comp.	X	R¹	R²	K		Col		Iso
7a	$COOCH_2$	H	H	·	<20	—	—	·
7b	$COOCH_2$	$OC_{10}H_{21}$	H	·	54	(·	47)	·
7c	$COOCH_2$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	·	41	(·	8)	·
8	CONH	$OC_{10}H_{21}$	H	·	47	·	66	·
9	CH_2OCH_2	$OC_{10}H_{21}$	H	·	<20	·	32	·

More recently it was proposed that the columnar phases of the polyamide **5** and the ester **6** are solely formed by the segregation of the polar groups from the non-polar aliphatic chains.[36,39] Thus, micro-segregation should be the main driving force for their self organisation with formation of liquid crystalline phases.

Interestingly, not only columnar phases were found. The diethylenetriamine derivative **4b,** for example, forms a smectic mesophase.[41,46,48] Cubic phases have been found for the short chain and the long chain diethylenetriamine derivatives **4a** and **4c** as well as for the triethylenetetraamine derivatives with higher chain lengths such as **3b**.[41] This indicates that in strong analogy to lyotropic systems and block copolymers the mesophase type is determined by a delicate balance of the relative space filling of the polar groups and the lipophilic chains.

3 Liquid crystals containing a tetrahedral or octahedral central core

Columnar mesomorphism was also found for organic molecules with a tetrahedral central core[37,49,50] such as **7**,[37] **8**[49] and **9**,[51] for octahedral metal complexes such as **13**,[52,53] for diabolo compounds such as **14**[54a] and dendrimers (*e.g.* compound **15**).[38,55]

We will focus our discussion on compounds **7–12**. The formation of these columnar phases was explained by a cylinder model as shown in Fig. 8 which was at first proposed for the mesophases of compounds **7**.[37] As evident from CPK-models of the pentaerythritol tetrabenzoates **7**, the tetrahedral linking unit inhibits the flat disc-like organisation of the taper-shaped

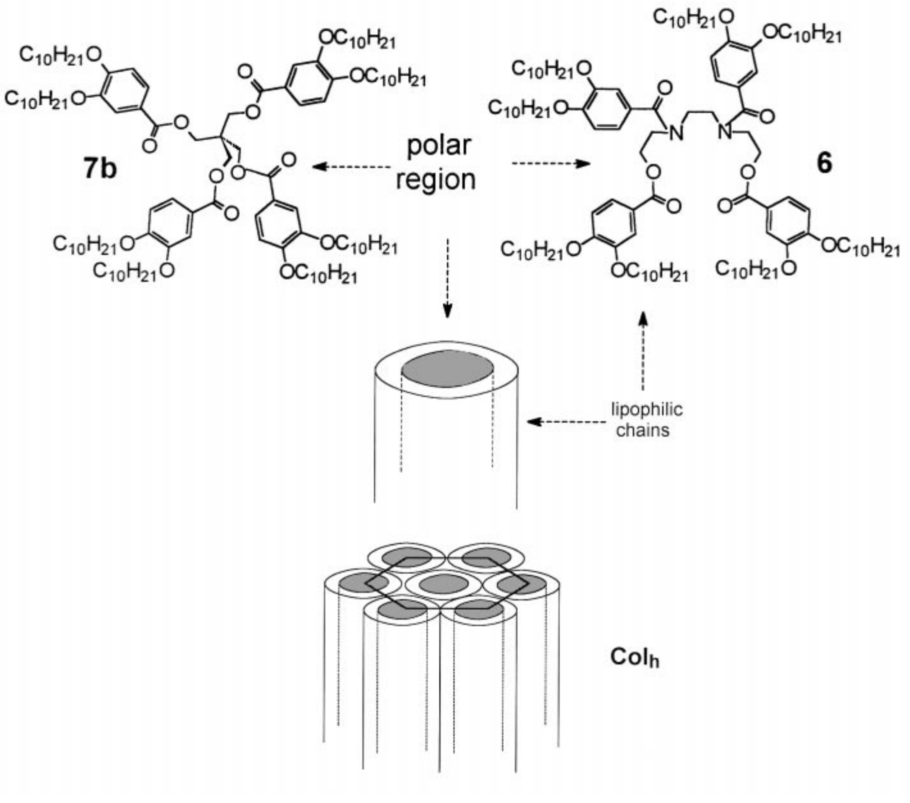


Fig. 8 Schematic of the organisation of compounds **6**[39] and **7b**[37] in their columnar mesophases

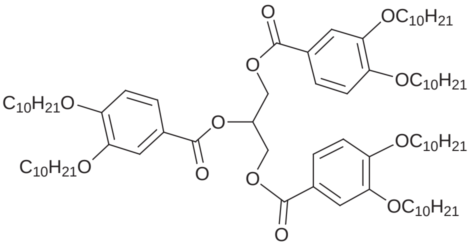
alkyl substituted aromatic units. Instead, these molecules can adapt different conformations with the alkyl chains more or less randomly distributed around the tetrahedral connecting unit and no particular anisometric shape is provided by the central unit. However, the accumulation of the polar groups (consisting of the carboxy groups, the aromatic rings and the ether-oxygens) gives rise to a distinct polar region in the centre of the molecules. The polar regions of different molecules interact preferably with each other and thus segregate from the aliphatic chains into separate domains (see Fig. 8).[37] During the process of self organisation the conformation of the individual molecules is influenced. Conformers with a rather flat shape should be favoured over other conformers, because they enable the most efficient interaction of their polar regions with neighbouring molecules. Thus, the supermolecular organisation of the molecules determines the actual molecular conformation. The relative space filling of the segregated regions and the pre-organisation of the lipophilic chains around the tetrahedral linking unit favour columnar aggregates.

The appearance of mesomorphic properties strongly depends on the number of chains. The most stable columnar phases were found for the 3,4-dialkoxybenzoates (*e.g.* compound **7b**). Introduction of an additional alkyl chain at each aromatic ring decreases the mesophase stability. The 12 alkyl chains of compound **7c** probably disturb the polar–polar interaction between neighbouring molecules.[37]

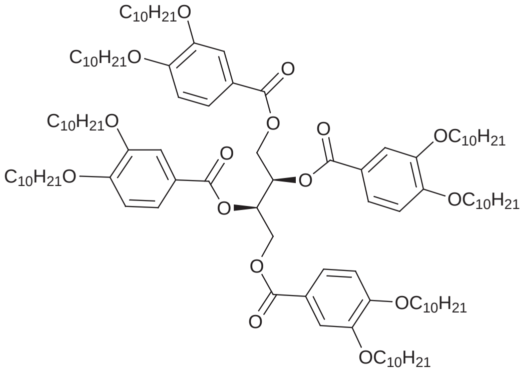
Also the peracylated D-threitol and D-mannitol derivatives **11** and **12** display columnar mesomorphism.[49] The increased clearing temperature of the D-mannitol derivative **12** in comparison to the D-threitol derivative **11** indicates that the mesophases can be stabilised by increasing the number of 3,4-dialkoxybenzoyl groups connected with each other. No liquid crystalline phases were found however on cooling the glycerol ester **10**.[49] It seems that irrespective of the particular shape of the molecules a minimum number of at least four 3,4-dialkoxybenzoyl groups must be connected to achieve liquid crystallinity.

The mesophase stability can be enhanced by increasing the intramolecular polarity contrast. For example, the replacement of only one CH_2OOC group of compound **7b** by an amide group (additional hydrogen bonding in compound **8**) raises the clearing temperature of the columnar mesophase[49] (a similar comparison can be made between the linear compounds **6** and **3a**). Replacement of one carboxy group of compound **7b** by a less polar CH_2O group however (compound **9**) lowers the mesophase stability.[51]

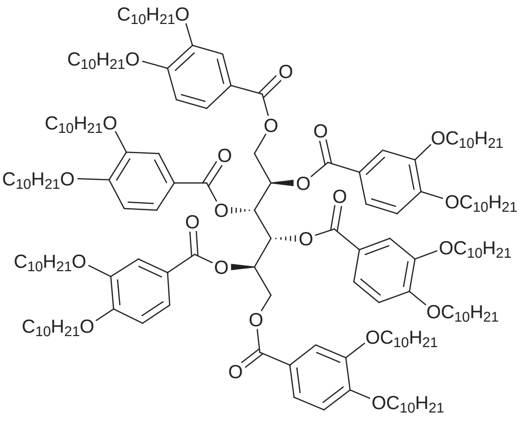
Also the mesophase formation by dendritic 3,4-dialkoxybenzamides such as **15**[38] has been described as mainly resulting from micro-segregation. Additionally, the liquid crystallinity of the octahedral metallomesogens **13** and diabolo liquid crystals (*e.g.* compound **14**)[54a] should be mainly due to micro-segregation of the polar cores from the lipophilic alkyl chains. Micro-segregation should also contribute to the special properties of main-chain and side-chain liquid crystalline polymers incorporating rod-like, disc-like and taper-shaped mesogenic units.[12,35]



10 K 98 Iso



11 K 44 (Col 40) Iso



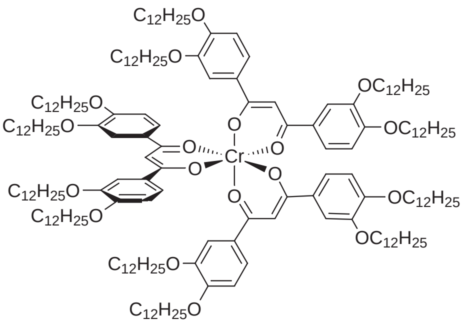
12 K <20 Col 55 Iso

Transition temperatures ($T/°C$) of peracylated glycerol, D-threitol and D-mannitol derivatives[49]

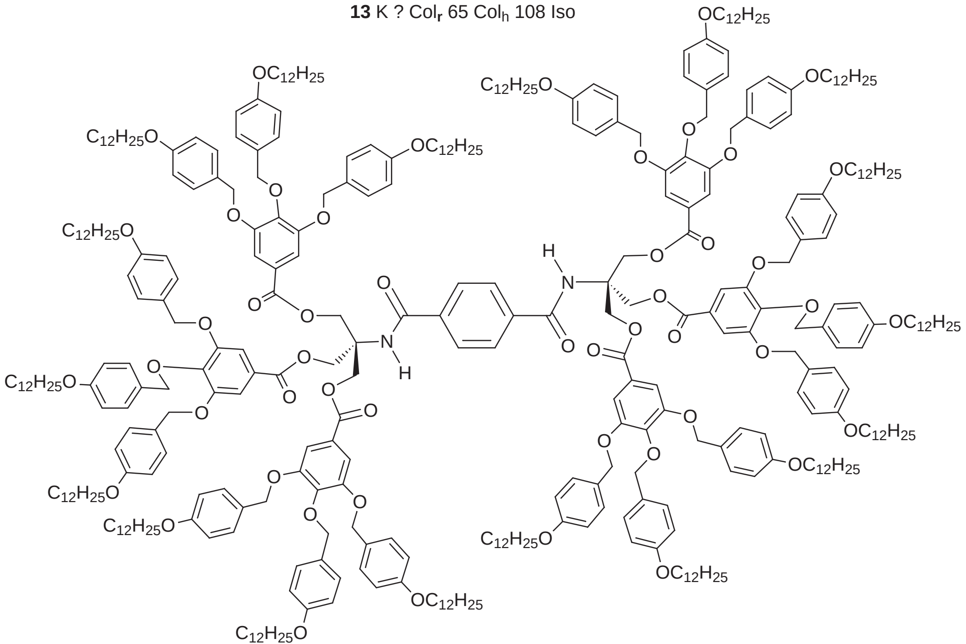
4 Polyhydroxy amphiphiles

An interesting family of liquid crystals is provided by the polyhydroxy amphiphiles, such as diols[11a,56–61] (*e.g.* compound **17**[58]), polyols, such as compound **18**[62] and the large family of carbohydrate mesogens[63] (*e.g.* compounds **19**,[64] **20**[65] and **21**[66]). Here distinct polar regions are formed by the dynamic liquid-like hydrogen bonding networks between the OH groups, which separate from the lipophilic *n*-alkyl chains.[67] A special feature of these compounds is that the amphiphilicity can be varied over a wide range depending on the number of hydroxy groups. Furthermore, these compounds are typically amphitropic mesogens[11a] forming not only thermotropic, but also lyotropic mesophases on addition of protic solvents.[57–60]

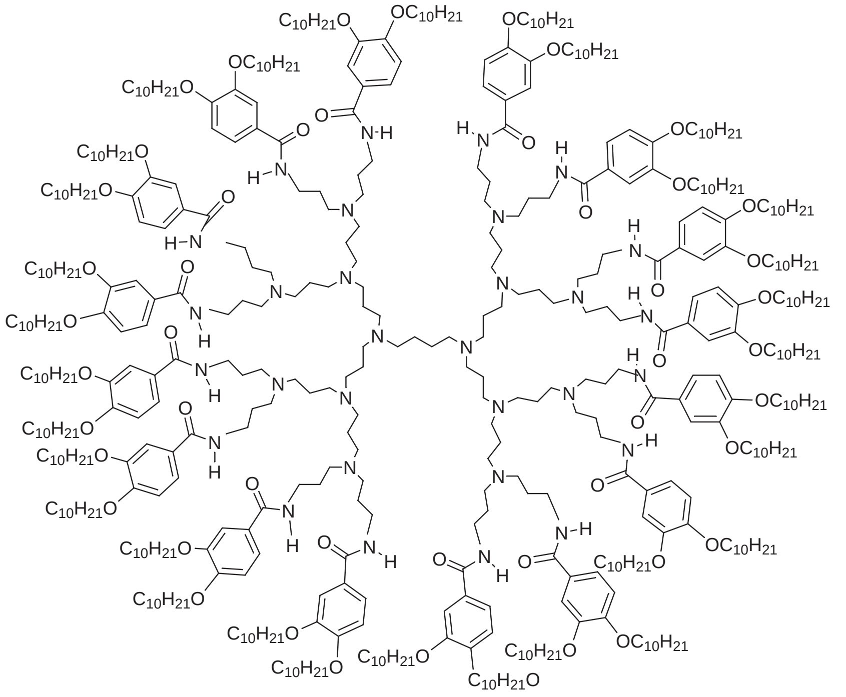
As a generally accepted rule at least two OH groups are necessary for the occurrence of liquid crystalline phases.[58,61] Simple primary alcohols (*e.g.* compound **16**)—despite the fact that they are amphiphilic and can for example form monomolecular films at interfaces[68]—do not form thermotropic or lyotropic mesophases. However, they can be turned into mesogens by introduction of additional hydroxy groups close to the first OH group. As obvious from Table 2, the stability of the thermomesophases continuously increases on increasing the number of hydroxy groups (diols < tetraols ~ monosaccharides < disaccharides). This shows that a certain polarity is necessary for micro-segregation in these small molecules. It seems that hydroxy groups can give rise to micro-segregation with formation of mesophases only if a sufficiently large number of them are connected side by side forming a distinct polar region (diol, carbohydrate unit) beside the lipophilic region of the alkyl chains. In other words, the fixation of several OH groups close to each other enables them to act co-operatively and increases the competition between the antagonistic molecular parts. In this respect the polyhydroxy amphi-



13 K ? Col$_r$ 65 Col$_h$ 108 Iso



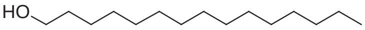
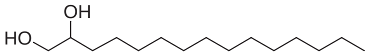
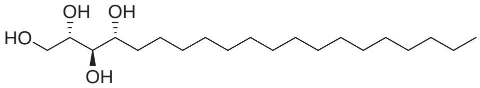
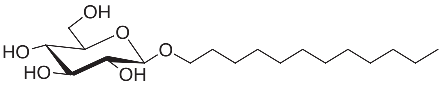
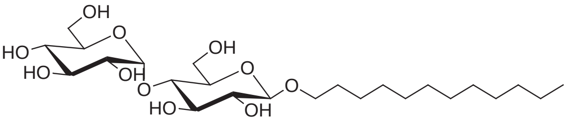
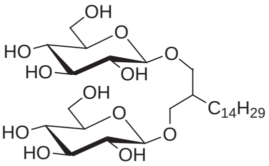
14 K<20 Col 150-152 Iso



15 K 76 Col$_h$ 124 Iso

Transition temperatures (T/°C) of representative low-aspect ratio mesogens: octahedral metallomesogens **13**[53b] (approximate values taken from a bar graph), diabolo mesogen **14**[54] and dendrimer **15**[38]

Table 2 Transition temperatures (T/C) of the thermotropic mesophases of selected *n*-alkyl-substituted polyhydroxy amphiphiles (**17**,[58] **18**,[62] **19**,[64] **20**,[65] **21**[66]). Abbreviations L_β = lamellar mesophase with rigid hexagonal ordered alkyl chains; for the other abbreviations see Fig. 3.

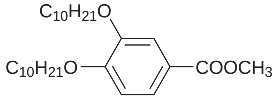
No.	Compound	Transition temperatures, T/°C
16		K 56 Iso
17		K 68 (L_β 65) Iso
18		K 108 S_A 156 Iso
19		K 80.4 S_A 143.4 Iso
20		K 102 S_A >245 Iso
21		K 111 Cub 205 Iso

philes can also be regarded as block molecules consisting of a hydrophilic oligo(hydroxymethylene) block and a lipophilic oligo(methylene) block. It should be mentioned here that in all polyhydroxy amphiphiles the hydrogen bonding leads to strong cohesive forces in the polar regions which reinforces micro-segregation and produces temporary cross-links between the individual amphiphile which also contribute to mesophase stability.

The block molecules described in the preceding sections bridge the gap between classical small mesomorphic (amphiphilic and anisometric) molecules and block copolymers. What we can learn is the following: if chemically different units are distributed in a molecule in such a way that two or more different regions are formed, then micro segregation can result. As in block copolymers the micro-segregation can be observed below a certain order–disorder temperature, which corresponds to the the transition from the liquid crystalline phase to the isotropic liquid (clearing temperature). It depends on the size of the blocks and on the degree of difference between the blocks. If the blocks are very large as in copolymers even very small differences of the chemical structure give rise to micro-segregation at ambient temperature (*e.g.* branched and non-branched hydrocarbons). If the blocks get smaller, the chemical difference between the blocks must be enhanced in order to maintain the ability to segregate. In classical amphiphiles a single ionic head group is sufficient. In polyhydroxy amphiphiles at least two OH groups are necessary and in non-dendritic ester compounds probably at least four —COO— groups must be combined.

5 Taper-shaped amphiphiles

The pentaerythritol tetrabenzoate **7b** can be described as a tetramer composed of four 3,4-dialkoxybenzoate units linked together. The ethyl 3,4-didecyloxybenzoate **22**[69] which represents a monomeric segment of the liquid crystalline compound **7b** is non-mesomorphic.



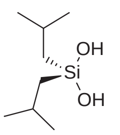
22 mp 43 °C

If the ester group of **22** is replaced by more polar groups, such as a polyhydroxy group, a stronger amphiphilicity is generated and liquid crystalline properties can be found for these small molecules. The formation of columnar mesophases by small taper-shaped amphiphilic compounds was described for several different polyhydroxy compounds. Probably the first compound of this type was diisobutylsilanediol **23**.[70] Selected examples of other taper-shaped polyhydroxy amphiphiles[61,63,71–74] are shown.

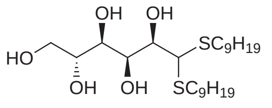
In most of these compounds the aliphatic chains were grafted directly onto the polyhydroxy groups of the polar moieties. In this way the number of attractive hydrogen bonds is reduced and therefore a larger number of alkyl chains often leads to the loss of mesogenity. The penta-*O*-hexyl-*myo*-inositol **27a**[75] and the tri-*O*-alkyl-D-glucose derivative **28b**[72] for example, do not display thermotropic behaviour.

In other cases the lipophilic alkyl chains were not directly attached to the polyhydroxy unit, but connected *via* an aromatic linking unit.[18,60,76–81] This allows the number of hydrogen bonds to remain constant whereas the size of the hydrophobic region can be gradually changed by variation of the number and the length of the grafted alkyl chains.

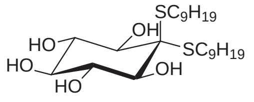
In this way the same diversity of different mesophases as observed in lyotropic systems and in block copolymers can be realised in thermotropic mesophases of pure *cis*-3,5-dihydroxycyclohexanes (*e.g.* compounds **29**, **30**),[60,80] 2,3-dihydroxypropylamides (compounds **31, 32**),[76,78] glucamides (*e.g.* compounds **33–35**), and *N*-methylglucamides.[18,76,78] Selected examples are shown. Single chain compounds form exclusively S_A-phases.[82] Double chain compounds can form smectic (S_A), bicontinuous



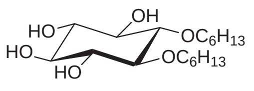
23 K 88.4 Col 98.7 Iso



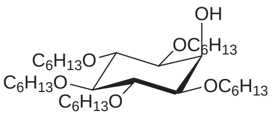
24 K 101.6 Col 125.8 Iso



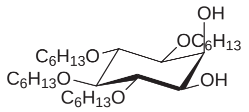
25 K 143.2 (Cub 129.9) Col 178.6 Iso



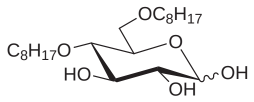
26 K 111.5 $\mathrm{Col_h}$ 167 Iso



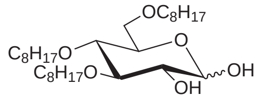
27a liquid



27b K 27.7 $\mathrm{Col_h}$ 35.8 Iso

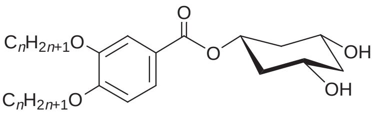


28a K 97 (Col 87.5) Iso

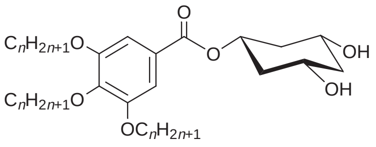


28b syrup

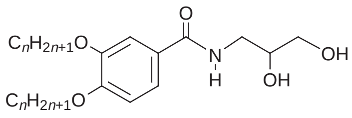
Phase transition temperatures (T/°C) of selected taper shaped polyhydroxy amphiphiles **23**,[70] **24**,[71] **25**,[74] **26**,[61] **27b**,[73a] **28a**[72] and **28b**[72] and the alcohol **27a**[75]



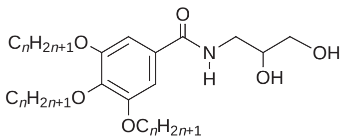
29a $n = 5$ K 73 ($\mathrm{S_A}$ 66.5) Iso
29b $n = 8$ K 63 (Cub 63) $\mathrm{Col_h}$ 95.5 Iso[a]
29c $n = 12$ K 79.5 $\mathrm{Col_{h2}}$ 124 Iso



30 $n = 12$ K 55 $\mathrm{Col_{h2}}$ 67 Iso



31 $n = 12$ K 98 $\mathrm{Col_{h2}}$ 148 Iso



32a $n = 6$ K 49 $\mathrm{Col_{h2}}$ 91 Iso
32b $n = 8$ K 59 $\mathrm{Col_{h2}}$ 74 $\mathrm{Cub_{I2}}$ 85 Iso
32c $n = 12$ K 69 $\mathrm{Cub_{I2}}$ 126 Iso

Phase transition temperatures (T/°C) of selected taper shaped polyhydroxy amphiphiles **29**,[80b] **30**,[60b] **31**[77] and **32**.[77] [a]Additional metastable liquid crystalline phases occur.

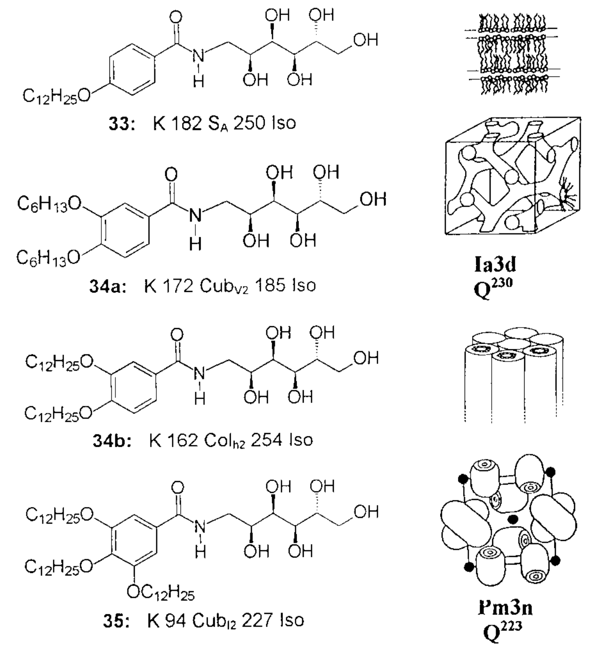


Fig. 9 Mesophases (transition temperatures, T/°C) of the N-benzoylamino-1-deoxy-D-glucitols **33–35** showing dependence on the number and length of the alkyl chains[18,76]

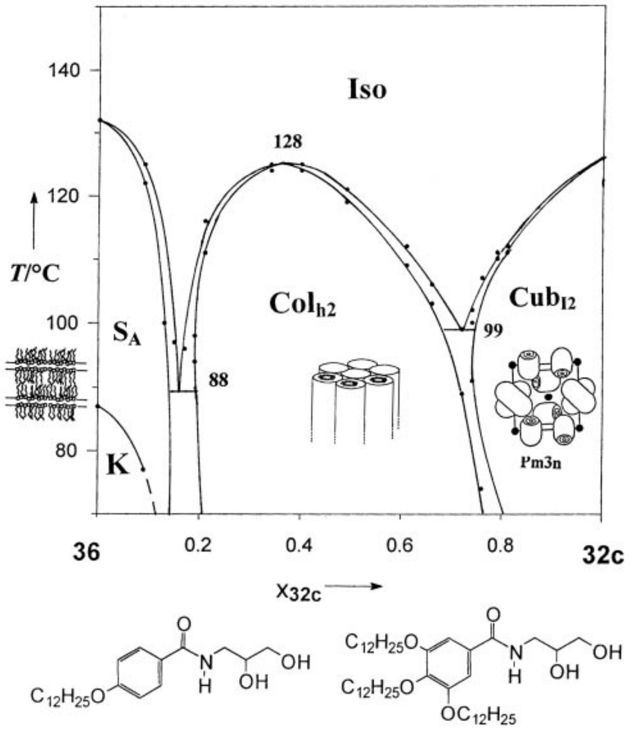
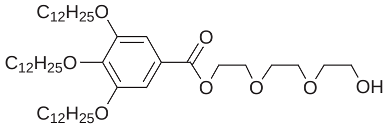
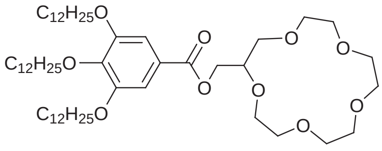
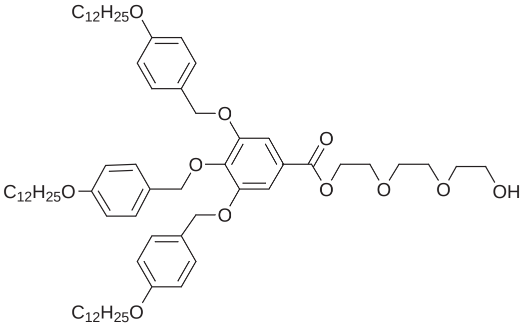


Fig. 10 Binary phase diagram of the system **32c–36**[78]

cubic ($\mathrm{Cub_{V2}}$) and columnar phases ($\mathrm{Col_{h2}}$), depending on the chain length and the size of the polar head group.[18,78,80] Triple chain compounds can form columnar ($\mathrm{Col_{h2}}$) and in some cases even micellar cubic mesophases consisting of closed spheroidal micelles ($\mathrm{Cub_{I2}}$).[18,76–78] Often, the type of mesophase can very simply be changed by adjusting the alkyl chain length and the size of the polar groups.[78] Thus, all main types of inverted (type 2) lyotropic mesophases have been realised as thermotropic analogues in the absence of any solvent, simply by tuning the relative size of the lipophilic and the polar regions.

Interestingly, this adjustment of the interface curvature can also be realised by mixing amphiphiles with different molecular shapes.[18,76,78] As an example, the binary phase diagram of the single chain compound **36** and the triple chain compound **32c**

Table 3 The influence of alkali metal triflates on the phase transition temperatures (T/°C) of the taper shaped polyether amphiphiles **37**,[86] **38**[87] and **39**[89]

No.	Compound	Transition temperatures of the pure materials, T/°C	Transition temperatures of the 1:1 complexes with triflates, T/°C
37		K 54 Iso	Li^+: K 46.5 Col_h 71 Iso
38		K 32 Iso	Na^+: K 69 (Col 27) Iso
39		K 56 Col_h 63 Iso	K 52 Col_h 134 Iso

is shown in Fig. 10.[78] In the contact region between the smectic phase of compound **36** (non-curved interfaces) and the micellar cubic phase of compound **32c** (interfaces are curved in two dimensions) a broad region of a hexagonal columnar mesophase is induced. This can be generalised. For example, it is also possible to obtain columnar mesophases by mixing structurally similar amphiphiles with bicontinuous (Cub_{V2}) and micellar cubic (Cub_{I2}) mesophases.[18,76,78]

Additionally, the size of the polar regions can be increased by interaction with protic solvents giving rise to a wide variety of lyomesophases.[18]

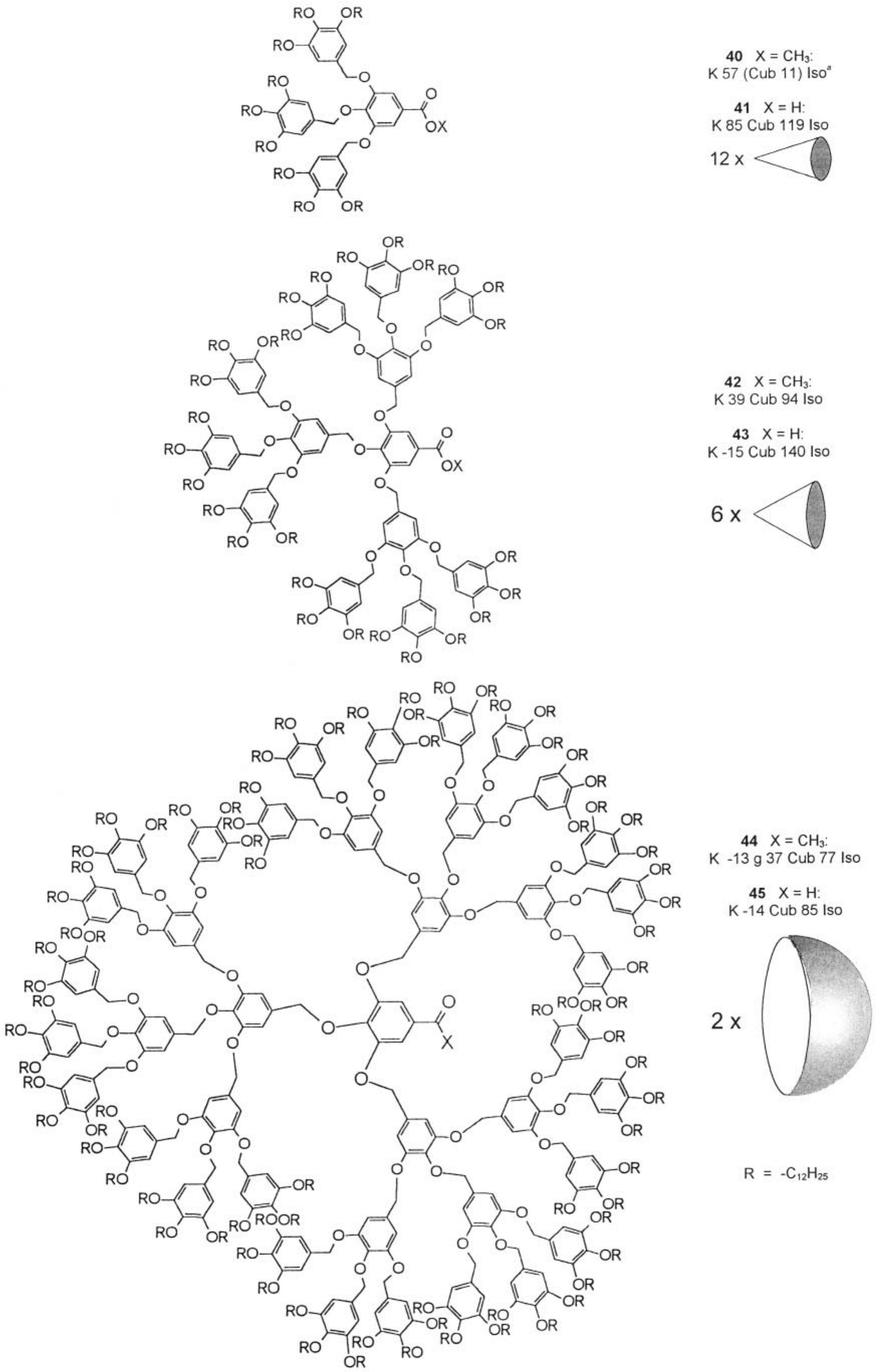
Remarkably, the mesomorphic properties of taper shaped amphiphiles are lost if the highly polar polyhydroxy groups are replaced by less polar groups, such as carboxy groups,[83] polyether chains or crown ethers.[35,84,85] As shown in Table 3, the oligo(oxyethylene) derivative **37**[86] for example is a crystalline solid. However, complexation of compound **37** with LiOTf results in a destabilisation of the crystalline phase and a spontaneous self-assembly into a cylindrical architecture which displays a hexagonal columnar mesophase.[86] The same result was found for the crown compound **38** on addition of sodium triflate.[87] Introduction of ionic interactions effected by the complexation of alkali metal ions by the polyether groups significantly increases the polarity contrast and probably also produces temporary crosslinks[88] between the individual molecules. This enables micro-segregation to occur with formation of columnar supermolecular aggregates.[35]

6 Wedge-shaped and cone-shaped dendrimers

Replacing the dodecyloxy chains of compound **37** (Table 3) by the 4-dodecyloxybenzyloxy chains increases the size of the polar regions of the taper shaped molecules and favours their micro-segregation. Compound **39**[89] for example forms a columnar mesophase despite the fact that only one hydroxy group is available for hydrogen bonding (see Table 3). Here, a rather large number of aromatic rings with their polar ether oxygen atoms are gathered close to each other. Together with the polyether chains, they create a distinct polar region which can segregate from the aliphatic chains.

Again, the shape of the polymolecular aggregates can be influenced by changing the relative size of the polar and lipophilic molecular parts. Thus, the methyl carboxylate **40** which has nine instead of only three lipophilic chains attached to the 3,4,5-tribenzyloxyphenyl core displays a monotropic cubic phase and the free acid **41** even has an enantiotropic cubic phase consisting of closed spheroidical micelles.[90] These molecules can be regarded as second generation dendrimers. The stability of the cubic phases was further increased on going to the third generation dendrimers **42/43** and decreases again for the fourth generation dendrimers **44/45**.[90] The model of their self-organisation is displayed in Fig. 12.[90] The number of dendritic molecules forming the individual micelles depends on the generation of the dendrons: 12, 6 and 2 monodendrons of generation 2, 3 and 4 respectively self assembled to one micelle. The cubic mesophases belong to the *Pm*3*n* space group, exactly the same space group as found for the supermolecular aggregates of the much smaller but more polar triple chain carbohydrate and diol derivatives such as **35**, **32b** and **32c**.[18,77,78] The dendrimers consist of large blocks and therefore a small segmental polarity contrast is sufficient to give rise to the formation of supermolecular aggregates. In the 3,4,5-trialkoxybenzamides **35** and **32b,c** the polarity contrast is much larger and therefore segregation can also occur with these much smaller molecules.

In classical amphiphiles, the chemical difference represents a hydrophilic/lipophilic contrast. However in a more general picture amphiphilicity describes any chemical or structural contrast within a molecule. Typical examples are hydrocarbon/fluorocarbon systems,[91] oligosiloxane/hydrocarbon[92] systems



40 X = CH_3:
K 57 (Cub 11) Iso[a]

41 X = H:
K 85 Cub 119 Iso

12 x

42 X = CH_3:
K 39 Cub 94 Iso

43 X = H:
K -15 Cub 140 Iso

6 x

44 X = CH_3:
K -13 g 37 Cub 77 Iso

45 X = H:
K -14 Cub 85 Iso

2 x

R = $-C_{12}H_{25}$

Fig. 11 Liquid crystalline properties (T/°C) of the cone shaped dendrimers **40–45**.[90] [a]Values taken from the first cooling scan.

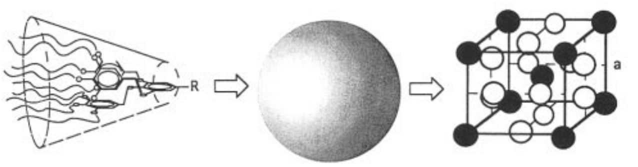


Fig. 12 Schematic presentation of the molecular self-organisation of cone shaped dendritic molecules to micellar cubic mesophases as adapted from ref. 90 (reprinted with permission from ref. 90, copyright American Chemical Society)

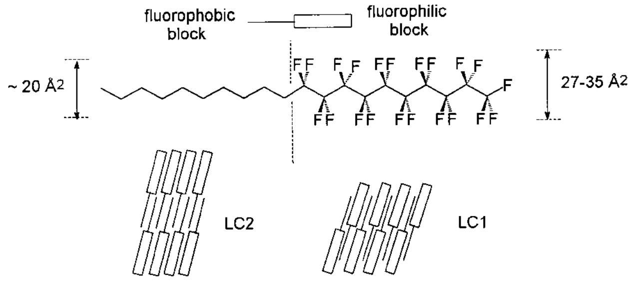
and also the rigid-core/hydrocarbon systems of calamitic and disc-like liquid crystals.

7 Mesogenic compounds with perfluorinated segments

It is possible to use the fluorophobic effect, which is the incompatibility of fluorinated and non-fluorinated hydrocarbons to induce liquid crystallinity.[91] However, there are some special properties of perfluorinated chains, which strongly influence their aggregation behaviour.[91] First, the cross-section area of a perfluorinated chain is 27–35 Å^2, which is large in comparison to alkyl chains (*ca.* 20 Å^2) and the cross-section area of biphenyl moieties (*ca.* 22 Å^2). Secondly, the perfluoroalkyl chain is more rigid.[91,93]

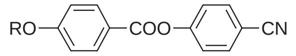
Partially fluorinated alkanes can be regarded as amphiphiles and as block compounds (see Fig. 13). The segregation of the fluorinated and the non-fluorinated blocks of these molecules into different domains is the main driving force for their interesting surfactant effects.[94] Thus, they can form normal and reversed micelles in perfluorinated solvents.[95] When mixed with hydrocarbon solvents organised gel-like structure can be found.[96] Furthermore, they represent the most simple thermotropic liquid crystals with smectic phases.[97] However, the different size of the fluorocarbon segments and hydrocarbon segments can give rise to liquid crystalline phases with partial interdigitation of the alkyl chains (LC1) or even to an antiparallel organisation of the molecules (LC2), an arrangement in which hydrocarbon chains and fluorocarbon chains are not segregated.[97]

Introduction of perfluorinated segments into classical calamitic liquid crystals[93,98–104] and also into discotic liquid crystals[105a] leads to a significant stabilisation of smectic and columnar mesophases, respectively. Nematic phases are generally suppressed. Also the mesomorphic properties of polycatenar compounds are significantly influenced by fluorination.[13,102] As in semifluorinated alkanes, the fluorophobic effect is in competition with steric effects due to the different size of the hydrocarbon and fluorocarbon chains. Thus, in the case of calamitic compounds antiparallel pairs or modulated smectic phases (*e.g.* $S_A{}^{\sim}$, columnar phases) are formed in order to avoid this steric stress.[93,99,102a]



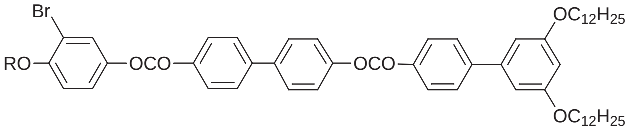
46 K ? LC2 46.9 LC1 63.3 Iso

Fig. 13 Liquid crystalline phases (transition temperatures T/°C) of partly fluorinated alkanes and model of their organisation in mesophases[97b] (LC1 and LC2 represent smectic phases)



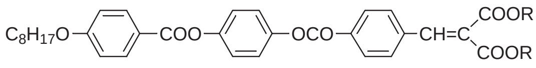
47a R = $C_{10}H_{21}$ K 40 N 157 Iso

47b R = $C_{10}F_{21}$ K 141 (S_c 138) S_A 167 Iso



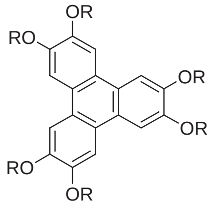
48a R = $C_{12}H_{25}$ K 120 Col_h 125 Iso

48b R = $(CH_2)_6C_6F_{13}$ K 105 Col 137 Cub 171 Iso



49a R = C_8H_{17} K 59 (S_c 53) S_A 84 N 94 Iso

49b R = $(CH_2)_2C_6F_{13}$ K 116 S_c 153 S_A 161 Iso



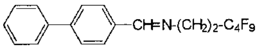
50a R = C_5H_{11} K 69 Col_h 122 Iso

50b R = $CH_2COO(CH_2)_2C_6F_{13}$ K 30 Col_h 210 Iso

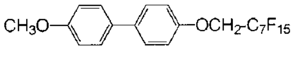
Selected examples for the influence of fluorination on the liquid crystalline properties (T/°C) of calamitic (**47a** *vs.* **47b**)[98] polycatenar (**48a**, **48b**),[13] swallow-tailed (**49a**,[102b] **49b**[102a]) and disc-like (compound **50a**[105b] *vs.* **50b**[105]) molecules

Some calamitic compounds incorporating fluorinated segments (polyphilic molecules) have been synthesised in order to use the micro-segregation to get non-chiral liquid crystals with ferroelectric properties (longitudinal ferroelectricity).[106,107]

Complete segregation was found for calamitic compounds with only one fluorinated chain and without a long alkyl chain. In the smectic E-phases of compounds **51**[103] and **52** [104] the rigid cores are completely interdigitated and ordered in an orthorhombic cell, but the perfluorinated chains remain liquid-like disordered (see Fig. 14). Here, the stress caused by the different space filling of the intercalated aromatic cores (2 × 22 Å^2) and the non-intercalated perfluoralkyl chains (27–36 Å^2) is released by folding the perfluoralkyl chains.



51 K 25 S_E 48 S_A 68 Iso



52 K 72 S_E 138 S_A 168 Iso

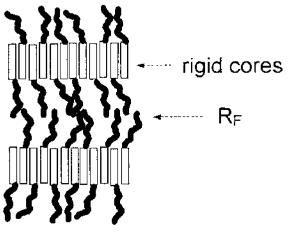
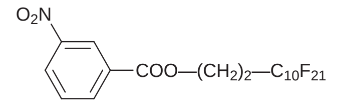
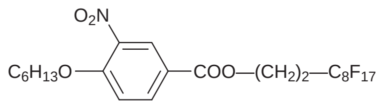


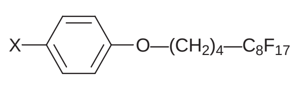
Fig. 14 Mesomorphic properties of calamitic mesogens **51**[103] and **52**[104] incorporating fluorinated segments (transition temperatures T/°C) and model of their arrangement in the smectic layers



53a K 62 S 92 Iso



53b K 44 S 49 S_A 51 Iso



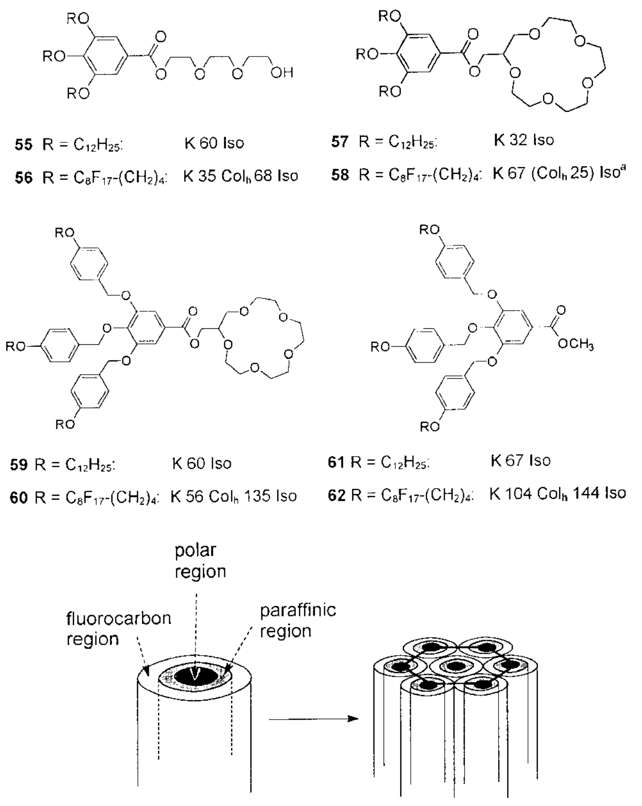
54a X = CN K 72 S_A 73 Iso
54b X = CH_2OH K 91 (S_A 81) Iso
54c X = $COOCH_3$ K 69 S_A 81 Iso
54d X = OCH_3 K 67 Iso

Selected examples of fluorinated liquid crystalline compounds **53**[108b] and **54**[108c] incorporating only one phenyl ring (transition temperatures T/°C)

Appropriate molecular design using the fluorophobic effect also allows the formation of smectic liquid crystalline phases for molecules with a single aromatic ring[108] which is a non-mesogenic rigid core in related nonamphiphilic hydrocarbon compounds. Both micro-segregation and the rigidity of perfluoralkyl chains should contribute to this effect. Increasing the chain-length and the amount of perfluorination increases the mesophase stability. A micro-segregated bilayer arrangement with a maximal overlap of the perfluorinated segments has been proposed.[108c] Using this concept mesogenic properties can be realised for simple alcohols (*e.g.* compound **54b**), which are non-mesogenic if combined with hydrocarbon residues. It seems however, that at least one polar substituent at the aromatic ring is necessary for mesophase formation. Replacement of the $COOCH_3$ group of compound **54c** by the less polar OCH_3 group (compound **54d**) for example causes the loss of mesogenic properties.[108c] Obviously, a certain degree of intramolecular contrast and/or a certain strength of the cohesive forces are necessary for mesophase formation in this class of compounds. Remarkably, no nematic phases have been found for these mesogens, which reveals that micro-segregation is the main driving force for their mesogenity.

A dramatic stabilisation of hexagonal columnar mesophases by semifluorination of the alkyl groups of taper-shaped amphiphiles was recently reported.[109–111] In contrast to the hydrocarbon analogues of the same size, which are non-mesogenic, the fluorinated tapered molecules can self-assemble into tubular supramolecular architectures. The columns consist of a central polar segment, the region of the lipophilic melted alkyl chains and the fluorocarbon-rich outer surface (see Fig. 15).

Using the fluorophobic effect columnar mesophases could also be obtained by rather small, non-dendritic taper shaped crown compounds (compounds **58** and **60**)[111] and even for non-dendritic carboxylates such as **62**.[111] Their non-fluorinated analogues are not liquid crystalline. Thus the fluorophobic effect can be used in combination with other incompatibilities to increase the segregation tendency. In some cases the fluorophobic effect alone can be sufficiently strong to induce molecular self-organisation replacing H-bonding and ion mediated complexation. Therefore it should be possible that less polar functional moieties (donor–acceptors, NLO compounds) can be used as part of the cores of the supermolecular columns.[111]



55 R = $C_{12}H_{25}$: K 60 Iso
56 R = C_8F_{17}-$(CH_2)_4$: K 35 Col_h 68 Iso
57 R = $C_{12}H_{25}$: K 32 Iso
58 R = C_8F_{17}-$(CH_2)_4$: K 67 (Col_h 25) Iso[a]
59 R = $C_{12}H_{25}$: K 60 Iso
60 R = C_8F_{17}-$(CH_2)_4$: K 56 Col_h 135 Iso
61 R = $C_{12}H_{25}$: K 67 Iso
62 R = C_8F_{17}-$(CH_2)_4$: K 104 Col_h 144 Iso

Fig. 15 Induction of columnar mesophases in the nonmesogenic taper shaped molecules **55**,[86] **57**,[87a] **59**,[87a] **61**[54b] by the fluorophobic effect (compounds **56**,[110] **58**,[111] **60**,[111] **62**;[111] transition temperatures, T/°C) and schematic presentation of the organisation of the partly fluorinated taper-shaped molecules into columnar mesophases, adapted from ref. 110. [a]Iso-Col transition obtained from the cooling scan.

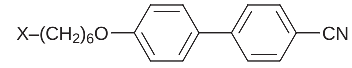
8 Liquid crystalline oligosiloxanes

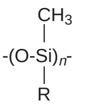
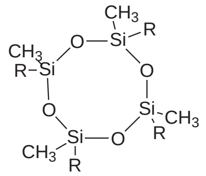
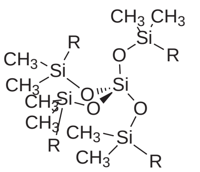
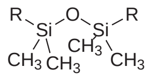
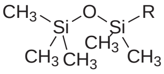
Polysiloxane side chain polymers represent an important family of liquid crystalline polymers.[12,112] By appending a mesogenic unit to a polysiloxane backbone, smectic phases are generally stabilised.

More recently cyclooligosiloxanes,[113] oligomeric[114] and dimeric liquid crystals with siloxane units[115,116] and calamitic molecules with oligosiloxane end groups[117] have also been synthesised. Selected examples of these compounds with 4-cyanobiphenyl rigid cores are collected in Table 4 and compared with the 4-cyano-4′-hexyloxybiphenyl **63**.[118] In contrast to this conventional calamitic mesogen, which forms a nematic phase, all compounds containing at least two siloxane units exhibit exclusively S_A-phases. It is especially remarkable that even the monomeric compound **68** is smectic despite the large size of the hexamethyldisiloxane end-group. Usually, such large branched moieties give rise to a loss of mesogenic properties or to a transition from smectic layer structures to less ordered nematic phases. The formation of a smectic layer structure in the case of the oligosiloxane derivatives **64–68** can be explained on the basis of oligosiloxane/hydrocarbon incompatibility, which gives rise to micro-segregation with layer formation. These smectogens can be regarded as triblock compounds containing three distinct parts: an aromatic core, a paraffin chain and a siloxane sub-group. Incompatible with each other these parts tend to locate themselves in three separate sublayers superposed in a partially bilayered S_A-structure as shown in Fig. 16.

A particularly efficient micro-segregation was found for LC polysiloxane copolymers with paired mesogens incorporating non-mesogenic dimethylsiloxane groups such as compound **69**. These copolymers show liquid crystalline behaviour up to a relatively high content of the nonmesogenic dimethylsiloxane

Table 4 Comparison of the phase transition temperatures (T/°C) of 4-cyano-4′-hexyloxybiphenyl **63**[118] with a related polysiloxane **64**,[112] the oligosiloxanes **65**,[116] **66**,[114] **67**[116] and the disiloxane substituted monomeric compound **68**[117]



No.	X	Transition temperatures, T/°C
63		K 57 N 75.5 Iso
64		g 14 S_A 166 Iso
65		g 57 S_A 118 Iso
66		g −14.7 S_A 118.7 Iso
67		K 86 S_A 91 Iso
68		K 46 S_A 53.8 Iso

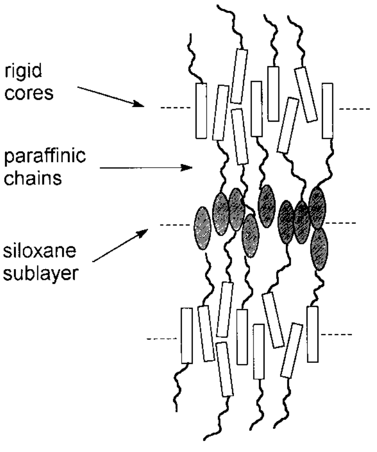
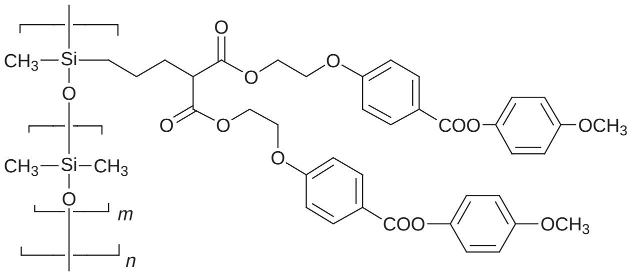


Fig. 16 Organisation of oligosiloxane containing liquid crystals in the smectic layers (adapted from ref. 116)

units in relation to the paired mesogens. For these diluted copolymers a distinct micro biphasic behaviour has been observed with two distinct glass transitions.[119] Some of these copolymers can take up significant amounts of decamethyltetrasiloxane, which can be incorporated in the polysiloxane sublayer[119] in a way analogous to the way water is incorporated between the polar groups of detergents to give lyotropic mesophases.

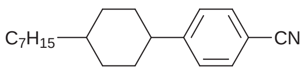


69

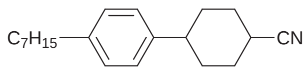
9 The importance of micro segregation for calamitic thermotropic mesogens

The importance of the distribution of polar and non-polar structural units within calamitic mesogens for the formation of nematic and smectic phases is a long known fact.[120] As a general rule polar and aromatic rigid units should not be interrupted by aliphatic or cycloaliphatic segments. Compounds **70** and **71**, for example, differ exclusively in the position of the lipophilic cyclohexane ring.[121] In the liquid crystalline compound **70** polar and lipophilic regions are well separated. In the nonmesogenic[122] compound **70**, however, the lipophilic cyclohexane ring separates the polar nitrile group from the polar aromatic ring.

Besides the molecular geometry and special conformational effects[123] micro-segregation should also contribute to this effect. Generally, micro-segregation is favoured in molecules with a well-defined intramolecular contrast, *i.e.* in compounds with distinct polar/rigid and less polar/flexible segments. Here, smectic liquid crystalline phases should be stabilised. If these different regions are mixed up, the stability of the liquid crystalline phases decreases.



70 K 30 (S 17) N 59 Iso



71 K 34 [N -25] Iso

Mesomorphic properties can also be lost if the rigid core is interrupted by flexible units. For example, no mesomorphic properties have been obtained for low molecular weight liquid crystals incorporating highly flexible mesogens such as diphenylethanes. These molecules can adopt a rod-like conformation and also bent conformations. However, main-chain polymers in which these flexible mesogenic units are connected *via* aliphatic spacers can form an interesting polymorphism (see Fig. 17).[124] A hexagonal columnar phase is observed, with the columns extended in the chain direction and with no positional order along the columns. On lowering the temperature the hexagonal order remains, but segregation of the alkyl chains from the aromatic parts sets in and an additional longitudinal order is established, which causes a transition into a smectic layer structure (S_B-phase).

It is often argued that the parallel organisation of the rigid cores of rod-like molecules is the main reason for their liquid crystallinity. However, only the formation of nematic phases is strictly bound to the rigid anisometric shape of the individual molecules. The formation of smectic layers is mainly driven by micro-segregation. Indeed, the rigid calamitic units provide an intramolecular contrast to the flexible aliphatic chains usually attached to them. It is well known that smectic phases are stabilised on elongation of the terminal aliphatic chains.

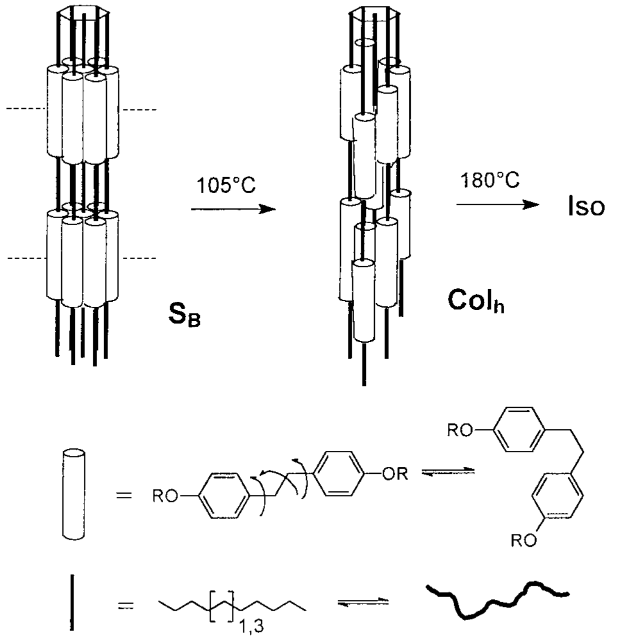
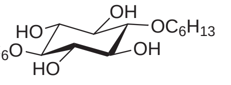
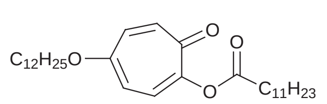


Fig. 17 Model of the S_B-phase and hexagonal columnar mesophase of main chain polymers with flexible mesogenic units[124]

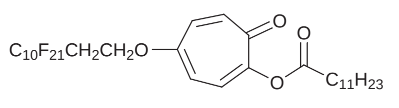
Starting with a certain length of the flexible aliphatic chains, the rigid cores and aliphatic chains segregate into different regions with formation of interfaces. Due to the approximately equal diameter of these two units in most cases non-curved aggregates (smectic layers) result. Additionally, the topology of the connection of the flexible chains to the ends of the rigid units provides a distinct pre-orientation of these chains and in this way the formation of smectic layers is additionally favoured. However, a calamitic rigid core is not necessary for a layer-like organisation. The lamellar phases of (single chain) polyhydroxy amphiphiles and ionic amphiphiles are well known examples for smectic phases formed by amphiphilic molecules without rigid cores.



72 K 144.8 S_A 176.9 I

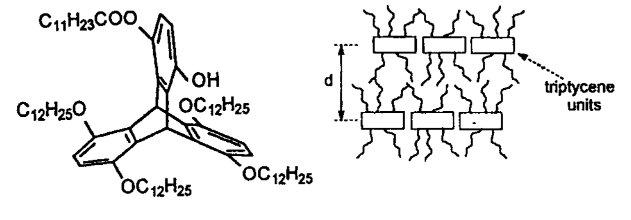


73a K 58 (S_A 45) Iso



73b K 101 S_A 127 Iso

Furthermore, appropriate molecular design using micro-segregation also allows the formation of smectic phases for molecules with a single aromatic or aliphatic ring which themselves do not represent mesogenic units. An example of a smectic compound with only one ring is provided by the *myo*-inositol ether **72**.[73b] Here, the hydroxy groups form a polar region which segregates from the lipophilic chains. Additionally, attractive forces are provided by hydrogen bonding which stabilise this arrangement. The 1,4-disubstitution pattern provides a linear pre-organisation of the alkyl chains. Therefore this compound exhibits a smectic A-phase of the monolayer type instead of the columnar phase of the corresponding taper shaped 1,2-disubstituted molecules (*e.g.* compound **26**).



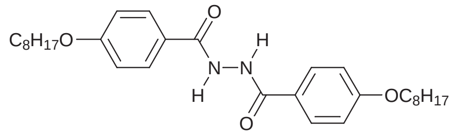
74 K ? S_1 39 S_2 156 S_3 163 S_A 168.8 Iso

Fig. 18 Transition temperatures (T/°C) and model of the smectic A-phase of the triptycene derivative **74**[127]

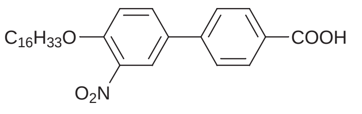
Monocyclic troponoids (compound **73a**) which have two alkyl chains, at least one of them connected *via* a carboxy group with the central tropone core also show monotropic S_A-phases.[125] Here, the polar tropone unit together with the linking groups form a distinct polar region, which segregates from the aliphatic chains. The S_A-phases can be further stabilised by the fluorophobic effect (compound **73b**).[126]

The recently described triptycene derivative **74**[127] represents another nice example of a non-classical smectic liquid crystal ('epitaxygen'). In this compound, five aliphatic chains were grafted laterally to a bulky triptycene core in such a way that they are pre-organised parallel to each other. This compound displays several smectic mesophases with unexpected high transition temperatures. The segregation of the aromatic triptycene core from the aliphatic chains and additional lamellar pre-organisation of the aliphatic chains due to the topology of their connection with the triptycene unit are probably the most important driving forces for mesophase formation.

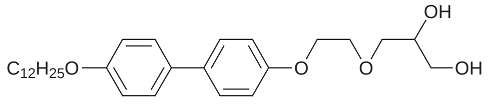
Another point which should be discussed here is the fact that, due to the preferred parallel arrangement of the rigid, rod-like units, the formation of curved interfaces is strongly hindered in the rigid calamitic mesogens. Thus, mainly layer structures can be found. Small differences between the space filling of the rigid cores and the pendant terminal chains can be compensated for by tilting the aromatic cores with respect to the layer normal, which gives rise to tilted smectic phases (*e.g.* S_C-phases).[128] In fact, fluid tilted phases (S_C-phases) have never been found in amphiphilic liquid crystals without rigid cores.



75 K 136.7 Cub 161 S_C 165 Iso



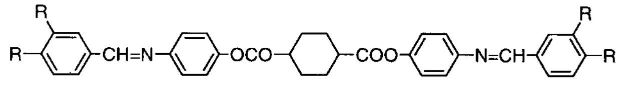
76 K 126.8 S_C 171 Cub 197.2 S_A 201.9 Iso



77 K 140 Col 146 S_A 169 Iso

In rare cases cubic[129,130] and columnar[131] phases can also be found for compounds with a rod-like shape (*e.g.* **75**–**77**), in many cases accompanied by S_C-phases. Interestingly, all these compounds incorporate highly polar groups in the core region or close to it and they have long alkyl chains. This probably enables a strong segregation and an especially efficient packing

Table 5 Mesomorphic properties (T/°C) of representative homologous polycatenar compounds **78a-c**[13a]



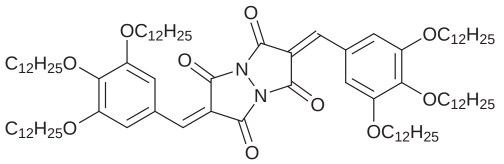
No.	R	Transition temperatures, T/°C
78a	OC_9H_{19}	K 146.5 S_C 268.5 Iso
78b	$OC_{11}H_{23}$	K 144 S_C 146 Cub 163 (Col_h 158) Iso
78c	$OC_{13}H_{27}$	K 141 Col_h 163 Iso

of the cores due to cohesive forces in the polar regions. A different space filling of the segregated regions may result and the smectic layers probably collapse with formation of ribbon-like segments to realise curved interfaces. Thus, the cubic mesophases could represent interwoven networks of these ribbons (Cub_V-phases).

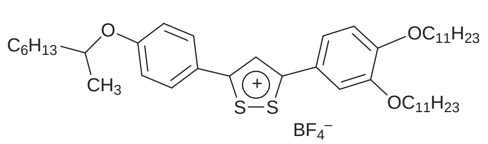
10 Polycatenar compounds

One way to obtain curved aggregates in mesophases of non-polar rigid calamitic molecules involves increasing the number of terminal aliphatic chains. Therefore, molecules with three, four, five or even six aliphatic chains attached to the termini of an extended rigid core, the so-called polycatenar compounds,[13] and molecules with branched terminal chains, the swallow-tailed compounds,[132] have been synthesised. However, in this class of compounds mesophases can only be obtained if the rigid parts are large enough to allow efficient segregation between the rigid units and the aliphatic chains. Furthermore, extended rigid cores enable sufficiently strong attractive interactions, which favour a parallel organisation. For example, molecules with five or six chains require a minimum of five and six rings, respectively.

The length of the rigid unit can be reduced, if additional attractive interactions are introduced and the intramolecular contrast is increased. Thus, columnar mesophases have been found for polycatenar tetrone derivatives[133] and for polycatenar ionic liquid crystals[134–136] (as for example compounds **79**[133] and **80**[136]) which contain significantly shorter but more polar rigid cores.



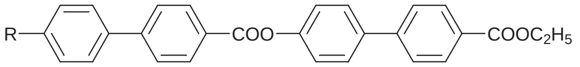
79 K 64 Col_r 112 Col_h 133 Iso

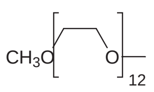
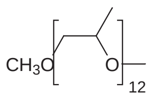


80 K 139 (Col_r 135) Col_h 154 N_{col} 178 Iso

Triple chain polycatenar compounds usually display nematic, smectic C-phases and other smectic low-temperature mesophases. Remarkably, no S_A-phases have been observed for pure polycatenar compounds with non-polar chains. The reason could be that small differences in space filling between the rigid cores and the pendant terminal chains can solely be compensated for by tilting the aromatic cores with respect to the layer normal. If, however, a certain difference in space filling of the segregated regions is reached, tilting of the molecules alone cannot sufficiently reduce this steric frustration. In these cases the layers break up into ribbon-like aggregates which can organise to bicontinuous cubic and columnar mesophases. Thus, smectic C, cubic (*Im*3*m* and *Ia*3*d*)[16] and columnar phases were found for tetracatenar compounds (Table 5), whereas exclusively columnar mesophases were observed for penta- and hexa-catenar molecules.

Table 6 Liquid crystalline properties (T/°C) of rod-coil molecules **81**[139] and **82**[137] and the influence of lithium triflate on the mesogenic properties of compound **81**[139]



No.	R	Transition temperatures, T/°C
81		K 135.2 S_A 148.1 Iso
	+0.2 eq. Li^+OTf^-	K 93.3 Cub 131.5 S_A 154.1 Iso
	+0.25 eq. Li^+OTf^-	K 92.8 Cub 137.2 Iso
	+0.3 eq. Li^+OTf^-	K 87.8 Cub 120 Col 126.2 Iso
	+0.4 eq. Li^+OTf^-	K 77.1 Col 120.5 Iso
82		K 21.5 Col 33.5 Iso

It should be pointed out that the same diversity of different mesophases as known for thermotropic and lyotropic phases of strongly amphiphilic molecules is found for these compounds. Only the formation of a micellar cubic mesophase has never been proven for polycatenar compounds. Because the formation of closed micelles requires a very large interface curvature, the occurrence of this type of mesophases seems unlikely in this class of compounds.

11 Rod-coil molecules

It is well known from the literature on low-molecular mass calamitic liquid crystals that the replacement of paraffin chains by oligo(oxyethylene) segments destabilises the thermotropic mesophases.[11a] The main differences with aliphatic chains are primarily the polarity of the oligo(oxyethylene) chains and secondly their higher flexibility and the preferred *gauche* conformation of the $-OCH_2CH_2O-$ units. Therefore, these chains can often adopt a helical conformation and occupy a significantly larger mean lateral area per chain than comparable aliphatic chains of the same length. Thus, smectic phases are strongly disturbed.

As in polycatenar compounds, mesomorphic properties can only be obtained by molecules with very large rigid segments. Recently, such rod-coil molecules have been synthesised. They consist of a large calamitic unit, connected to an extended flexible oligo(oxyethylene) chain.[137–139] As a result of the micro-segregation of the lipophilic and rigid cores from the flexible and polar polyether chains, these rod-coil molecules self assemble into well-defined microstructures, such as lamellar and columnar mesophases depending on the block composition (see Table 6).

Compound **81** for example forms a smectic A-phase which on addition of lithium triflate turns *via* an intermediate bicontinuous cubic mesophase into a columnar mesophase.[138] These phase transitions should be caused by the larger spatial requirement of the complexed coil segments in comparison with the non-complexed. Alternatively, the transition from a smectic to a columnar structure can be achieved by enlarging the coil segments by introduction of additional substituents in the polyether chain [*e.g.* the methyl groups in the oligo(propylene oxide) derivative **82**].[137]

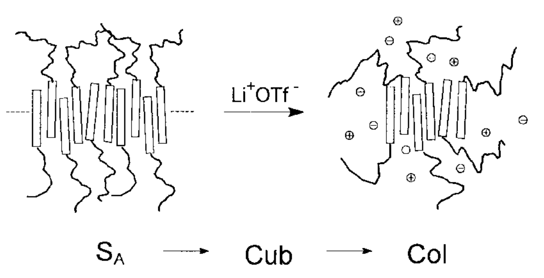
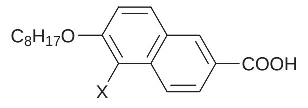


Fig. 19 Organisation of rod-coil molecules in the smectic and in the columnar mesophase (induced by LiOTf)[124]

12 Laterally substituted calamitic mesogens

It is well known that the connection of non-polar aliphatic chains to a calamitic rigid core at positions other then the terminal ones decreases the smectic mesophase stability (see Fig. 20).[120,140]

However, if polar groups are introduced in a lateral position on a calamitic mesogen, then the smectic phases can be stabilised, because these substituents can cause attractive intermolecular interactions and can increase the intramolecular polarity contrast between a central polar core and the lipophilic chains. The earliest example has been provided by the laterally substituted naphthoic acids **84** and **85**.[141] The smectic tendency of the chloro-substituted naphthoic acid **85** is remarkably high, whereas the naphthoic acid without the lateral chloro substituent **84** is only a nematic liquid crystal.



84 X = H K 161.5 N 190 Iso
85 X = Cl K 169 S_C 183 N 199 Iso

Other examples are given by *p*-terphenyl derivatives with lateral groups capable of hydrogen bonding.[142] The comparison given in Fig. 21 clearly reveals this. Increasing the number of possible hydrogen bonds raises the S_A-isotropic transition temperature despite the fact that the size of the lateral substituent is significantly enlarged. The smectic layers should be stabilised by both the attractive hydrogen bonding and the increased intramolecular polarity contrast between the central rigid cores and the terminal lipophilic chains.

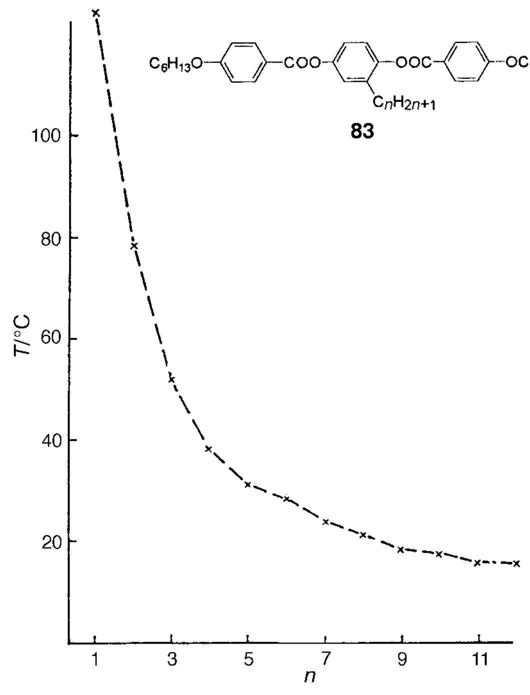


Fig. 20 Dependence of the thermotropic clearing temperatures of laterally substituted hydroquinone dibenzoates (*T*/°C) on the length of the lateral alkyl chain (adapted from ref. 140)

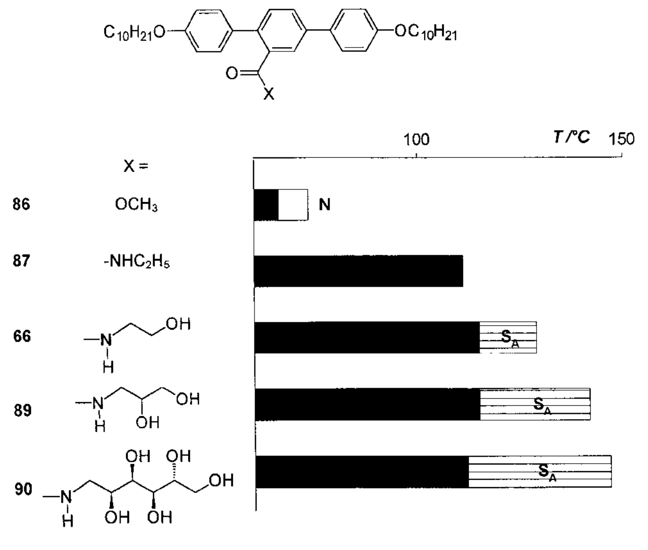


Fig. 21 Comparison of the thermotropic behaviour of methyl 2,5-bis(4-decyloxyphenyl)benzoate **86** with the 2,5-bis(4-decyloxyphenyl)-benzamides **87–90** with different sized lateral groups;[142] black areas represent the crystalline state

If the size of these polar lateral groups however is increased without simultaneously increasing the number of attractive hydrogen bonds, the smectic mesophases are destabilised. This is shown in Fig. 22 for the terphenyl derivatives with lateral polyether chains. Surprisingly, however, starting with the bis(oxyethylene) compound **93** a rectangular columnar mesophase can be observed.[143] A ribbon model was proposed for these columnar mesophases, which can be explained as follows. In the series of compounds **91–94**, the flexible lateral groups become more and more polar by elongation of the polyether chain. At a certain size and a certain degree of polarity the flexible and polar lateral groups start to segregate from the rigid and lipophilic terphenyl units into separate domains. This causes the smectic layers to collapse incompletely as the layers break up and form ribbons. These ribbons become ordered in a two-dimensional rectangular lattice. A possible model[143] is shown in Fig. 23.

The ribbons consist of parallel rigid *p*-terphenyl cores which

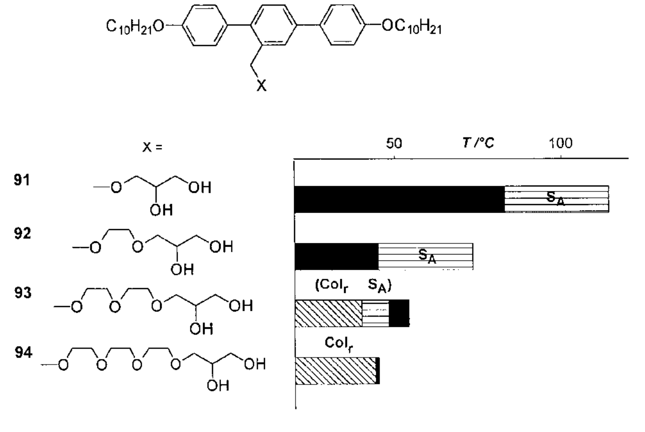


Fig. 22 Thermotropic liquid crystalline phases of the 2,5-bis(4-decyloxyphenyl)benzyl ether **91–94** with different length of the lateral oligo(oxyethylene) chains;[143] black areas represent the crystalline state; the mesophases of compounds **93** and **94** are monotropic

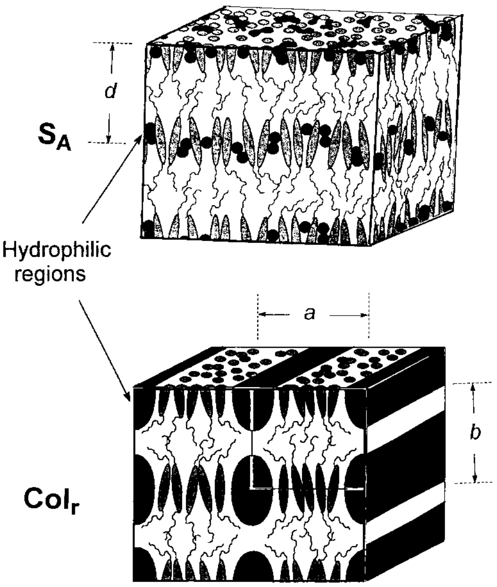
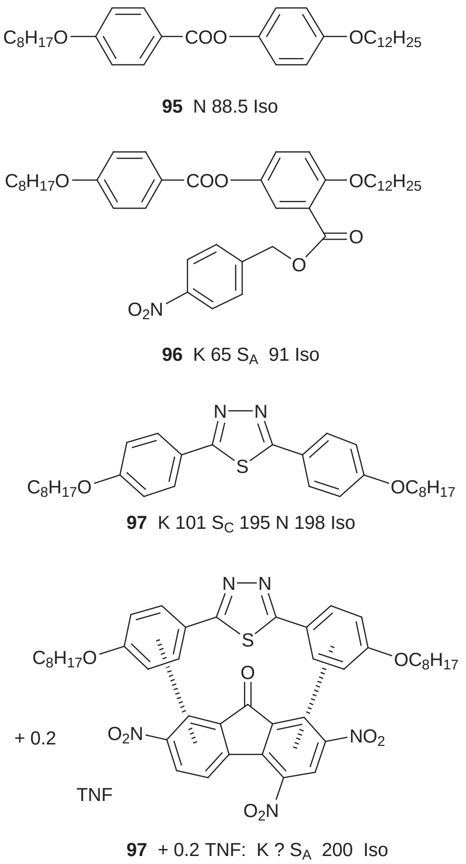


Fig. 23 Schematic illustration of the S_A-phase and the ribbon arrangement for the rectangular columnar phase (Col_r) of compound **93**.[143] The black areas represent the segregated regions of the polar groups. The polar groups of the molecules in the middle of the ribbons cross over the neighbouring calamitic terphenyl units.

are laterally separated by the hydrophilic domains of the lateral polyether chains. The alkyl chains are molten and fill up the space between the ribbons in the other dimension. This arrangement seems reasonable because it simultaneously enables the parallel organisation of the rod-like molecules and also the best segregation of polar and lipophilic units into separate regions. Thus, the mesophase should be composed of an alternating structure of different lamellae. The regions of the molten alkyl chains form one type of lamella. The other one is composed of ribbons of rigid *p*-terphenyl units laterally separated by cylinders containing the hydrophilic groups. The proposed model is related to that suggested for supermolecular structures which have recently been found in triblock copolymers consisting of three linearly combined blocks.[144] Here, besides other superstructures, lamellae with cylinders at the lamellar interfaces have been found.[145] Indeed, the molecules **93** and **94** can be regarded as low molecular weight three-block compounds composed of three different and incompatible blocks: the rigid cores, the flexible and lipophilic alkyl chains and the flexible but polar polyether chains. In contrast to linear triblock copolymers these Y-shaped block molecules have the cylinders located within one of the distinct layers instead of being located at their interface.

Protic solvents such as water and formamide can stabilise the columnar mesophases of compounds **93** and **94** and can induce novel columnar mesophases. For example, with formamide a columnar phase can be induced in the smectic phase of compound **92**. Up to three different rectangular columnar mesophases have been found for compound **94** with a long lateral polyether chain on increasing the water concentration.[131*b*,146] The increase in size and polarity of the lateral groups by hydration should facilitate micro-segregation and thus should be responsible for the stabilisation and/or induction of the columnar mesophases. Likewise, columnar lyomesophases have been induced by specific recognition of alkali metal ions by facial amphiphiles consisting of a 4,4″-didecyloxy terphenyl rigid core with laterally appended crown ether units.[146,147]



95 N 88.5 Iso

96 K 65 S_A 91 Iso

97 K 101 S_C 195 N 198 Iso

97 + 0.2 TNF: K ? S_A 200 Iso

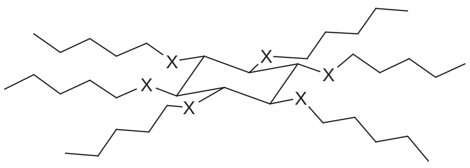
Selected examples of mesophase stabilisation (T/°C) by polar lateral substituents (nonsubstituted compound **95** *vs.* **96**) and by doping a 2,5-diphenylthiadiazole derivative (compound **97**) with the nonmesogenic electron acceptor TNF

Layer-like arrangements of calamitic molecules can also be stabilised by electron donor–acceptor (EDA) interactions between the rigid cores. For example, long chain derivatives of two-ring mesogens having an acceptor substituted phenyl ring in the lateral branch (*e.g.* compound **96**) exhibit enantiotropic smectic A phases. The mesophase thermal stability of these strongly branched derivatives can be higher than that of the laterally unsubstituted parent compounds (e.g. compound **95**) and nematic phases are replaced by S_A-phases.[148] Furthermore smectic A-phases can be induced by addition of the nonmesogenic electron acceptor trinitrofluorenone (TNF) to the nematic phases of calamitic molecules such as **97**.[149] Both attractive interactions provided by EDA-interactions and attractive quadrupole interactions[149*b*,150] and also the increased micro-segregation due to the enhanced polarity in the regions of the calamitic parts should contribute co-operatively to the observed mesophase stabilisation. In the systems **97**/TNF the length of the alkyl chains is of unusually great importance, whereby mesophase stabilisation is only found for long chain compounds. This can be explained by the fact that segregation is increased on increasing the size of the competing parts. Furthermore, the larger space requirement of the 'mixed' (compound **97** + TNF) polar regions necessitates a better space filling of the aliphatic regions by longer or branched[149*b*,151] alkyl chains.

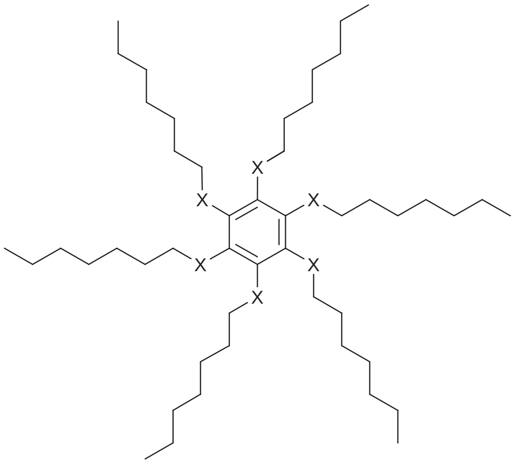
13 Influence of micro-segregation on mesophases of disc-like molecules

It seems that micro-segregation with creation of an interface between polar and non-polar regions is also one of the main driving forces for the appearance of liquid crystalline properties in disc-like compounds.

It has often been observed that columnar mesophases are lost, if polar groups in the centre of disc-like molecules are replaced by less polar ones.[34] For example, the inositol ethers and esters **99**, **100**[152] and the hexakis(alkylsulfono)benzene



98 X = CH$_2$, m.p. 66
99 X = O K 18.4 Col_{ho} 90.8 Iso
100 X = COO K 68.5 Col_{ho} 119.5 Iso



101 X = S liquid
102 X = SO$_2$ K 120 Col 138 Iso

The influence of the polarity in the central core of disc-like molecules on the columnar mesophase stability. Increasing the polarity (**98** < **99** < **100**;[152] **101** < **102**[154,155]) enhances the clearing temperatures

102[153,154] are mesomorphic compounds in contrast to the all-*trans*-hexaalkylcyclohexane **98**[155] and the hexakis(alkylthio)-benzene **101** which are non-mesogenic. Also it is well known that only acylated azamacrocyles (see section 2) are mesomorphic[44] whereas the corresponding alkyl derivatives are not[156] and this should largely be due to the higher polarity of the amide groups in comparison to the amino groups. This means that in these cases the micro-segregation also helps the columnar supermolecular structures to develop. This effect is especially important if the central core is rather small. A sufficient intramolecular polarity contrast and an efficient surrounding of the central cores by aliphatic chains are then necessary to obtain mesomorphic properties. Nevertheless conformational effects and the rigidification of the central regions may also contribute to this effect. However, we will not discuss this topic further because it will be incorporated in a feature article concerning columnar mesomorphism.[43] It is only pointed out that columnar ordering is not preliminarily caused by the flat disc-like shape of molecules, rather than by micro-segregation of the rigid cores from the flexible chains, by attractive core–core interactions and by the topology of connection of the lipophilic chains with the central unit. Thus columnar mesomorphism is not restricted to disc-like compounds. Columnar phases can also be found for molecules with non-discoid central cores such as tetrahedral pentaerythritol tetrabenzoates (compounds **7**) and octahedral metallomesogens (compound **13**). However, large flat and rigid cores can give rise to significantly attractive core–core interactions. Furthermore, they can significantly increase the intramolecular contrast and efficiently pre-organise the chains radially around this core.

14 Mesophases of more complex block compounds

Linear AB-diblock copolymers represent the most simple and best investigated block compounds. Related concepts can also be applied to multiblock copolymers, graft-copolymers, comb-copolymers, star-block copolymers *etc.* In the case of triblock copolymers[144] even more complicated supermolecular structures which are a combination of lamellae, cylinders and spheres such as helical morphologies,[158] lamellar structures with cylinders at the lamellar interface[145] and the ball at the wall structure[159] have been found.

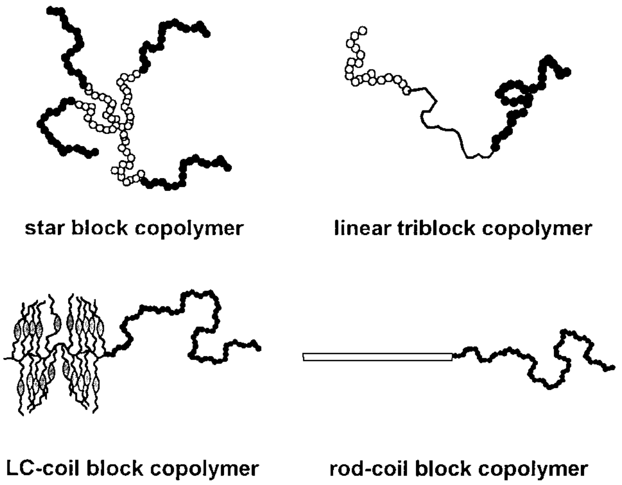


Fig. 24 Selected examples of more complex block copolymers

Interesting new morphologies can also be observed if the chain rigidity is increased for one block (rod-coil block copolymers).[160] In poly(hexyl isocyanate-b-styrene) diblock polymers smectic C-like and smectic O-like morphologies have been detected.[161] The morphology of these materials arises from the competition of the coil and rod blocks into mesoscopically ordered periodic structures and the tendency of the rod blocks to form anisotropic orientationally ordered structures. Many classical calamitic liquid crystals can be regarded as block molecules, *i.e.* as low molecular weight analogoes of rod-coil block copolymers. Interesting, new liquid crystalline phases could also be expected for low molecular weight block compounds, if rigid structures are combined with two or even more different and incompatible chains in different positions. First examples are provided by partly fluorinated liquid crystals (section 7), polyether amphiphiles with rod-like units (compound **77**) and calamitic compounds with laterally attached polyether chains (section 12).

Block and graft copolymers consisting of a coil block and a liquid crystal side chain polymer block have recently been reviewed.[162] These LC-coil diblock copolymers combine mesomorphic order with micro phase separation in a single polymer. Here molecular ordering occurs on two different length scales within one system. This offers unique possibilities to obtain new self-organised ordered systems in nanoscopic dimensions. Thus, the LC-subphase can influence the morphology of the polymer system,[163] and on the other hand the block morphology can stabilise the liquid crystalline subphases.[164] Completely new supermolecular structures, such as flat cylinders and hexagonal shaped cells, are also possible.[165]

15 Influence of chirality

It is well known that molecular chirality can give rise to helical supermolecular structures.[166] This is not restricted to nematic phases which are turned into cholesteric phases. Chirality can also modify positionally ordered mesophases by distortion of the interfaces. Examples are the twisted grain boundary (TGB) phases, the S_Q-phases (tetragonal phases)[167] and optically isotropic mesophases which represent distorted layer structures of calamitic compounds.[166a] Interestingly, a TGB phase has

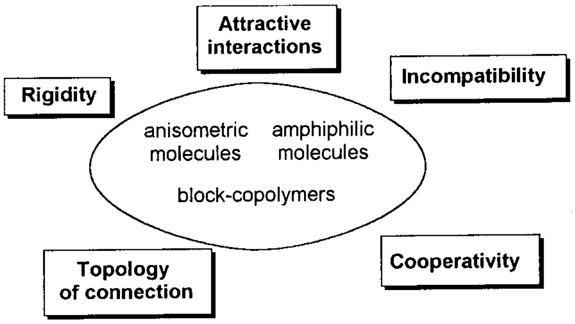


Fig. 25 The main driving forces of liquid crystallinity

also been found for a chiral block copolymer.[168] However, in systems with strongly competing parts, such as lyotropic and thermotropic mesophases of amphiphilic molecules no influence of chirality on the structure of fluid positional ordered mesophases has been detected yet.[169] For example no influence of chirality on the mesophases of amphiphilic carbohydrates and other chiral polyhydroxy amphiphiles could be measured.[63] Due to the strong competition between the antagonistic parts larger forces probably must be applied to affect their aggregate structure. In systems with a less pronounced intramolecular contrast (mesophases of nonamphiphilic but anisometric mesogens and weakly segregated block copolymers) even small changes can easily disturb the mesophase structure and also molecular chirality can affect the self organisation.

16 Summary

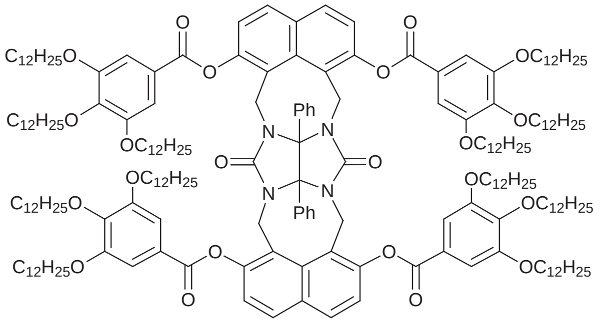
In summary, the unique properties of liquid crystals arise from the combination of order and mobility on a molecular level. The mobility is caused by the thermal motion of the molecules, whereas the order is provided by a combination of molecular anisometry, attractive forces and micro-segregation. Depending on the particular molecular structure one of these ordering forces can dominate. For example the nematic state is mainly caused by the anisometry of molecules or aggregates. Lyotropic systems of detergents or lipids are predominante organised by micro-segregation and attractive forces, whereas micro-segregation alone can be responsible for the mesophase formation of block copolymers and also for the mesomorphic properties of low molecular weight block molecules.

In this paper we have focused our interest on positionally ordered mesophases, smectic, columnar and cubic. This paper provides facts that establish bridges between the polymorphism of amphiphiles, rod-like molecules, disk-like molecules and block copolymers.

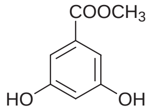
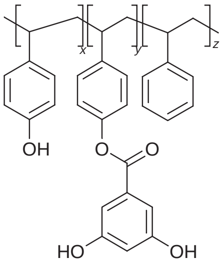
All molecules dealt with in this article are amphiphilic. The segregation of chemically different units (rigid, flexible, aliphatic, polar, perfluorinated, oligosiloxanes, *etc.*) leads to the formation of interfaces separating two or even more media. This micro-segregation depends on the degree of chemical and structural differences and the size of the different building blocks. If the different units are very large as in block copolymers even very small differences in chemical structure give rise to micro-segregation at ambient temperature. If the blocks are small, the chemical differences between blocks have to be increased.

At the same time, the molecules are mesogenic because they build up structures intermediate between disordered liquids and highly ordered crystals. The main feature of these mesophases is that they consist of chemically different regions separated in space by interfaces: planar interfaces in smectic phases, cylindrical interfaces in columnar phases and three-dimensionally bent interfaces in the cubic phases and other 3D-mesophases. The interfaces can either be well defined as in most lyotropic systems and in strongly segregated block copolymers or very hazy (sinusoidal) as for example in the case of S_A and S_C phases of calamitic compounds and weakly segregated block copolymers. This depends on the degree of competition between the segregated regions. Weakly segregated systems can easily be disturbed by chirality, by changing the molecular structure and by addition of solvents. Strongly segregated systems are significantly less sensitive. In many cases one of the segregated regions is liquid like (aliphatic chains or solvent) and the other one is more or less ordered or even crystalline (parallel arranged discs or calamitic units, quasi-crystalline layers of the ionic groups in the ribbon phases of pure soaps, *etc.*).[32,170] This additional order gives rise to a large number of different subphases as for example smectic low-temperature phases.[1]

Table 7 Mesomorphic properties of complexes between the glycouril derivative **103** and selected resorcinol derivatives[171]



103

Guest	Host-guest ratio	Transition temperatures, $T/°C$
none		K 159–164 (N 161) Iso
	10:3	K -3 S_1 82 S_2 131 Iso
	1:1	K -4 N 110 Iso
	1:1	K 30 Col 141 Iso

If the molecules are rigid the formation of flat (calamitic molecules) or cylindrical (disc-like molecules) interfaces is strongly favoured. When the molecules are flexible (amphiphiles, block-copolymers), then a wide variety of different mesophases can be found (lamellar, columnar, cubic and different intermediate phases). In most nonlamellar thermotropic mesophases of low molecular weight compounds the stronger cohesive forces are located inside the aggregates surrounded by lipophilic chains. It would be of interest to synthesise novel molecules which can form aggregates with the stronger attractive forces outside, as already realised in block copolymers and as is well known from the type 1 lyotropic surfactant–water systems. The first compound of this type is probably the carbohydrate derivative **21** (Table 2). Interesting new liquid crystalline phases could also be expected for novel low molecular weight block compounds which combine micro-segregation and molecular anisometry.

It can be expected that many more mesomorphic compounds with non-conventional molecular structures should be detected in the future. One example is represented by the mesomorphic glycoluril derivatives (*e.g.* compound **103**, see Table 7) and their complexes with resorcinol derivatives.[171] In this case micro-segregation should also be a main driving force for self-organisation.

Micro-segregation is also important in other fields. Thus, polymerisation reactions were found to be more facile in ordered melts in which the reactive moieties of the monomers are segregated and create a supramolecular reactor of an increased concentration of polymerisable groups.[172]

As only one example from the life sciences it should be mentioned that micro-segregation represents a fundamental driving force in protein folding.

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