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Formation of Columnar and Lamellar Lyotropic Mesophases by Facial Amphiphiles with Protic and Lipophilic Solvents

Jörg Andreas Schröter,[†] Carsten Tschierske,*[,†] Michael Wittenberg,[‡] and Joachim Heinz Wendorff[‡]

Contribution from the Institute of Organic Chemistry, University Halle, Kurt-Mothes Strasse 2, D-06015 Halle, Germany, and Institute of Physical Chemistry and Center for Material Science, University Marburg, 35032 Marburg, Germany

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Abstract: The influence of water, formamide, and *n*-dodecane on the liquid crystalline properties of several rodlike 4,4″-bis(decyloxy)-*p*-terphenyl derivatives incorporating nonionic hydrophilic groups in a central position was investigated by polarizing microscopy and X-ray scattering. Up to three different rectangular columnar mesophases have been found for molecules with large hydrophilic groups with increasing concentrations of protic solvents. Remarkably only one lattice parameter changes in dependence on the mesophase type and the number of solvent molecules coordinated to the polar groups. We propose that the columns represent ribbons consisting of the rigid terphenyl units, separated laterally by the segregated regions of the hydrophilic groups, whereby the three different columnar mesophases should result from an anisotropic swelling of the polar regions on addition of solvents. Lipophilic solvents (dodecane) destabilize the columnar phases and replace them by smectic layer structures (S_A phases).

Introduction

The formation of a wide variety of different supermolecular structures, such as thermotropic and lyotropic mesophases, micelles, vesicles, and ordered thin films, is a well-known feature of amphiphilic molecules consisting of a polar head group connected with flexible lipophilic chains, such as detergents and lipids. In addition to these classical amphiphiles, novel nonconventional amphiphiles such as gemini surfactants[1] and rigid spiro-tensides and -phospholipides[2] are of growing interest because they are characterized by unusual properties and novel supermolecular structures.

We have synthesized a novel class of nonconventional amphiphiles, in which the hydrophilic group is grafted in a position lateral to a rodlike rigid core.[3] Here, the tendency of the calamitic units to arrange parallel to each other is in competition with the segregation of the hydrophilic groups in distinct domains. This means that the two main driving forces controlling the self-organization are directed orthogonal to each other in these molecules. Such compounds are of interest because in some respects they resemble the amphiphilic pattern of certain biomolecules, such as cholic acid salts and facial amphiphilic peptides.[4] These amphiphiles are able to form well-defined thin films at the air−water interface as recently shown.[5] Additionally, in the pure state, they have an interesting polymorphism (see Table 1).[3a−c] Smectic layer structures were reported for compounds **1a,b,** whereas rectangular columnar

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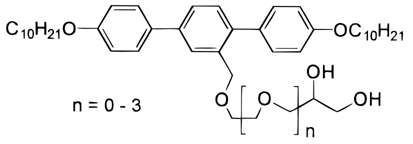

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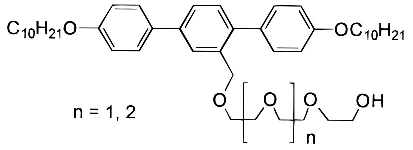

mesophases (Col_r) were found for compounds **1c,d**, in which the *rac*-2,3-dihydroxypropyl groups are connected via polyether chains with the terphenyl rigid core.[3b] For these columnar mesophases a ribbon structure as shown in Figure 1 was proposed.[3b] The ribbons should consist of the parallelly arranged rigid *p*-terphenyl cores which are separated by the segregated hydrophilic domains of the rather large, flexible, and polar lateral groups. The lipophilic alkyl chains are molten and fill up the space between the ribbons. This arrangement enables a parallel organization of the rodlike molecules and also a segregation of polar and lipophilic units into separate regions. In this contribution we report the influence of protic and of lipophilic solvents on the mesophase behavior of this novel type of amphiphilic compounds.[6]

[†] University Halle.

[‡] University Marburg.

* Fax: (0345) 55 27030. E-mail: coqfx@mlucom6.urz.uni-halle.de.

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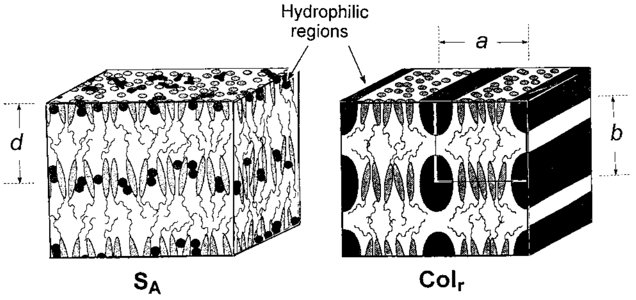

Figure 1. Schematic illustration of the S_A phases of compounds **1a**−**c** (the polar regions, indicated by black dots are randomly distributed within the layers of the rigid cores) and of a possible ribbon arrangement for the rectangular columnar phases (Col_{r1}) of compounds **1c**,**d**.[3b] The black areas represent the phase-separated regions of the polar groups. The polar groups are sufficiently large that the molecules in the middle of the ribbons can cross over the neighboring calamitic terphenyl units and are incorporated in the polar segregated regions.

Table 1. Thermotropic Phase Transition Temperatures (T/°C) of Compounds **1** and **2**[a]

compd	n	K		Col_{r1}		S_A		Iso
1a	0	•	83	–	–	–	114	•
1b	1	•	66	–	–	–	73	•
1c	2	•	54	(•	40	•	48)	•
1d	3	•	45	(•	40)	•	–	•
2a	1	•	61	–	–	(•	52)	•
2b	2	•	44	–	–	(•	31)	•

[a] Abbreviations: K = crystalline solid, N = nematic phase, S_A = smectic A phase, Col_{r1} = rectangular columnar mesophase, Iso = isotropic liquid).[3]

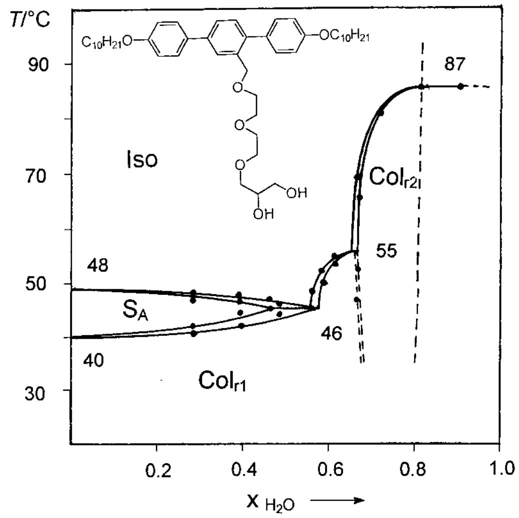

Figure 2. Binary phase diagram of compound **1c** with water.[6]

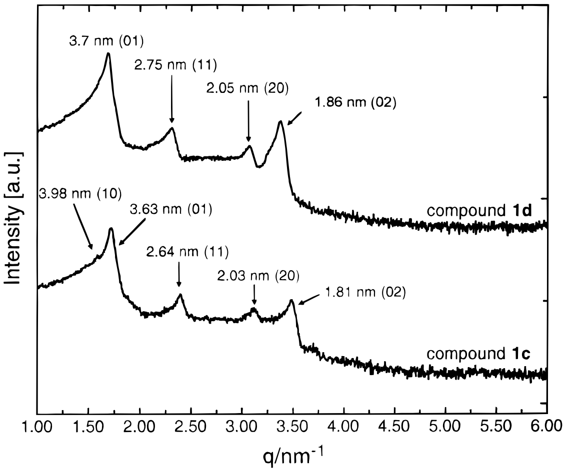

Figure 3. Small-angle region of the X-ray scattering diagrams of the lyotropic mesophase of the water-saturated sample of compound **1c** at 80 °C (Col_{r2}) and of the lyotropic mesophase of the water-saturated sample of compound **1d** at 60 °C (Col_{r3}).

Materials and Methods

The synthesis and the thermotropic mesophase behavior of compounds **1** and **2** have been described recently[3] (see Table 1). All compounds **1** are racemic mixtures. Solvent-saturated samples as well as the formation of mesophases in the contact region between the pure compounds and the solvents (water, formamide, and *n*-dodecane) were studied as a function of concentration by polarizing microscopy. Binary mixtures of selected compounds were investigated in more detail by calorimetry, and binary phase diagrams were established. Finally, the water-saturated samples of selected compounds were sealed in capillaries and investigated by small-angle X-ray scattering using a Kratky compact camera.

Results

A. Oligo(oxyethylene) Derivatives with Terminal 1,2-Diol Groups. Mesomorphic Properties in the Presence of Water. At first we will consider the diol derivatives **1a**−**d.** The smectic phase of compound **1a,** which has the *rac*-3,4-dihydroxy-2-oxapentyl group directly attached to the rigid core, is obviously not influenced in the contact region with water. Probably, this rather small hydrophilic group is shielded by the lipophilic residues and is not able to take up water. The other compounds **1b**−**d** incorporating at least one oxyethylene unit take up water more readily. The smectic A phase of **1b** is slightly stabilized in the contact region with water (clearing temperature of the water saturated sample T_{cl} = 84 °C), whereas the S_A phase of the bis(ethylene glycol) derivative **1c** is destabilized and replaced by other mesophases at higher water concentrations.

The phase diagram of the binary system of compound **1c** with water is shown in Figure 2. The pure compound has a S_A−Col_{r1} dimorphism. An increase of the water content gives rise to a destabilization of the smectic A phase and to a stabilization of the rectangular columnar phase. At a water content of ca. two molecules water per molecule diol **1c** (X_{H_2O} = 0.67), another mesophase occurs, which is significantly stabilized on further increase of the water content. The maximum of the water uptake amounts to a ratio of approximately four molecules water per molecule of **1c** ($X_{H_2O} \approx 0.8$).

The mesophase of the water-saturated compound **1c** was investigated by X-ray scattering. A diffuse scattering in the wide-angle range indicates that the mesophase is a phase without long-range order. A smectic phase of higher order can therefore be excluded. The peaks in the small-angle region can unambiguously be assigned on the basis of a rectangular 2D lattice (see Figure 3). The lattice parameters amount to a = 4.02 nm and b = 3.63 nm (at 80 °C). The lattice parameter a is nearly identical with the corresponding value of the columnar phase of the pure compound **1c** (a = 4.04 nm and b = 3.44 nm at 39 °C),[3b] whereas only the parameter b is enlarged. Thus, in dependence on the water content, there are two different rectangular columnar phases Col_{r1} and Col_{r2}. The numbering of the columnar phases is arbitrary according to the order of their appearance with increasing solvent content (there is no relation with the descriptors of direct and inverted mesophases in conventional lyotropic systems). Col_{r1} occurs in the water free sample and is stable up to a water content of ca. 2 mol of water/mol of diol. It displays a spherulitic texture (see Figure 4a) and has a rather low viscosity. The second rectangular

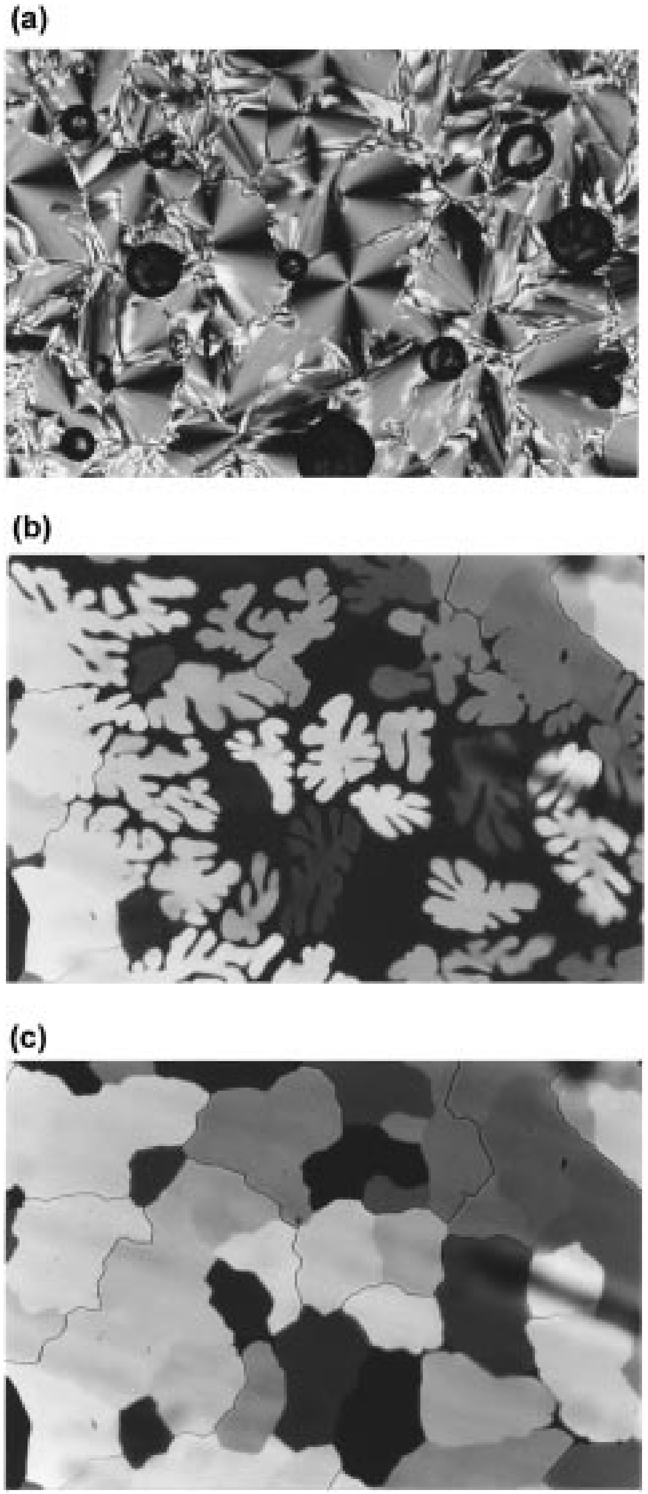

Figure 4. Optical photomicrographs of the mesophases of compound **1c** (crossed polarizers). (a) Spherulitic texture of the Col_{r1} phase at 39 °C obtained by cooling from the S_A phase. (b) Fern-like texture at $T = 87$ °C of the lyotropic Col_{r2} phase of the water-saturated sample as obtained on cooling from the isotropic state. (c) Mosaic-like texture of the Col_{r2} phase at $T = 83$ °C.

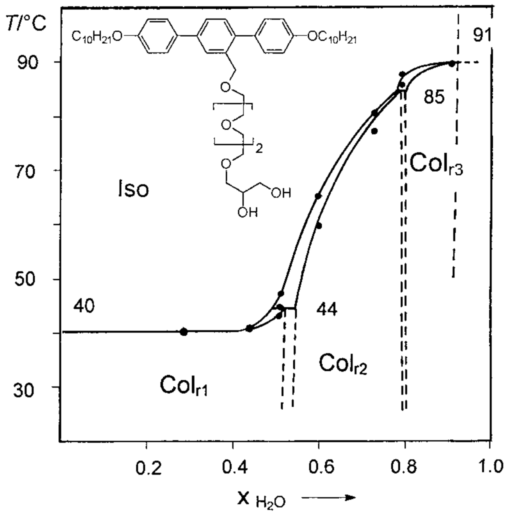

Figure 5. Binary phase diagram of compound **1d** with water.

columnar phase Col_{r2} is formed in the presence of more than 2 mol of water/mol of diol **1c,** and it displays a mosaic-like texture consisting of differently colored plates (Figure 4c). Some of these regions appear completely black without birefringence, which points to a perpendicular orientation of the optical axis with respect to the surface of the microscope slides. This excludes a tilted arrangement of the molecules in this phase. Furthermore, this columnar phase has a significantly higher viscosity than the Col_{r1} phase.

The binary phase diagram of the **1d**/water system is shown in Figure 5. The pure compound **1d**, which incorporates one more oxyethylene unit than **1c** has exclusively a rectangular columnar thermotropic mesophase (Col_{r1}). In the contact zone with water two new mesophases are induced. The Col_{r2} phase, which shows the same mosaic-like texture as the Col_{r2} phase of **1c**, already appears at a water content of ca. 1 mol of water/mol of **1d** ($X_{H_2O} = 0.55$). An additional phase (Col_{r3}) is formed at $X_{H_2O} = 0.8$, which corresponds to a ratio of approximately four molecules water per molecule of amphiphile. It displays a spherulitic fan texture. This mesophase can take up a maximum of about 11 molecules water per molecule of **1d**.

The water-saturated sample of **1d** was investigated at 60 °C by X-ray diffraction. The diffraction pattern of the Col_{r3} phase is of the same type as the one of the Col_{r2} mesophases of compound **1c** (see Figure 3). This mesophase is consequently also a rectangular columnar mesophase (Col_{r3}). The lattice parameter amount to $a = 4.1$ nm and $b = 3.7$ nm (at 60 °C). Again, only the parameter b is enlarged and the lattice parameter a is nearly identical with the corresponding lattice parameter of the columnar phase (Col_{r1}) of the pure compound **1d** ($a = 4.15$ nm, $b = 3.18$ nm at 39 °C).[3b]

It is really surprising that independent of the water content all investigated columnar mesophases of compounds **1c**,**d** display rectangular 2D lattices which differ only in one of the lattice parameters.[7]

Mesophases in the Presence of Formamide. The mesophases of the new amphiphiles can also be influenced by using formamide as a protic solvent. The S_A phase of **1a** is slightly destabilized (clearing temperature of the S_A phase of the formamide-saturated sample $T_{cl} = 103$ °C). The principal phase diagrams of the binary mixtures of compounds **1b**−**d** with formamide are shown in Figure 6. Because these simplified phase diagrams were obtained from contact preparations, they can give only a qualitative picture of the phase behavior in dependence on the solvent content. Again, the S_A phases of **1b**,**c** are destabilized; the columnar phases on the other hand are always stabilized. The phase diagram of compound **1d** with

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[7] A rectangular columnar mesophase ($a = 4.1$ nm and $b = 2.9$ nm) was also found for a lyotropic system consisting of a 4,4″-bis(decyloxy)-*p*-terphenyl derivative with a lateral 18-crown-6 unit and 1 M aqueous KBr: Schröter, J. A.; Tschierske, C.; Wittenberg, M.; Wendorff, J. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1119.

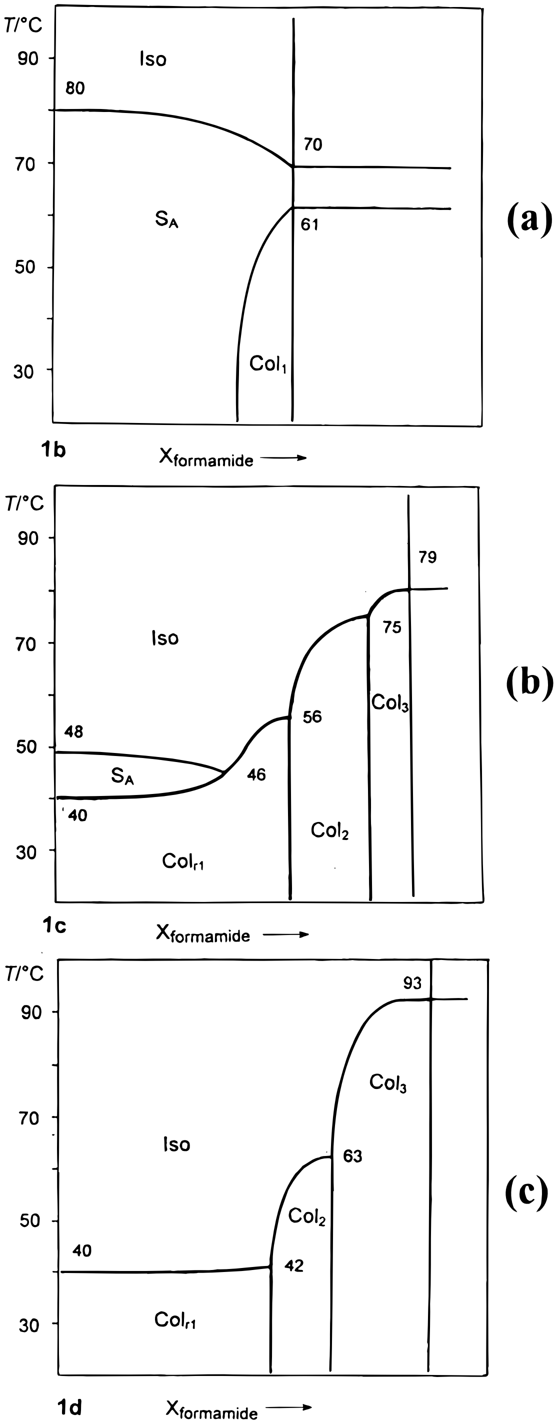

Figure 6. Simplified principal phase diagrams of compounds **1b**−**d** with formamide as obtained by investigation of the contact regions between crossed polarizers. Col$_1$ = columnar mesophase with spherulitic texture; Col$_2$ = columnar mesophase with mosaic-like texture; Col$_3$ = columnar mesophase with spherulitic texture.[8]

formamide (Figure 6c) is very similar to that with water (Figure 5). In both cases, three different mesophases were observed and their textures are identical with those of the corresponding phases in the **1d**/water system (Col$_1$ = spherulitic, Col$_2$ = mosaic-like, Col$_3$ = spherulitic). Therefore, we can assume also that these mesophases are columnar mesophases.[8] The only difference between these two phase diagrams is that the Col$_3$ phase is more dominant in systems containing formamide. It seems that formamide favors the formation of columnar mesophases more strongly than does water. The stabilization of the Col$_3$ phase by formamide is also obvious from comparison of the phase diagrams of the compound **1c** with formamide (Figure 6b) and with water (Figure 2). Only in the case of the formamide-saturated samples of compound **1c** is the Col$_3$ phase detected. Furthermore, a columnar mesophase can be induced by formamide in the case of the ethylene glycol derivative **1b**, which has exclusively the S$_A$ phase as pure compound and in the presence of water. This induced columnar phase displays the same spherulitic texture as observed for the Col$_{r1}$ phases of **1c**,**d**.

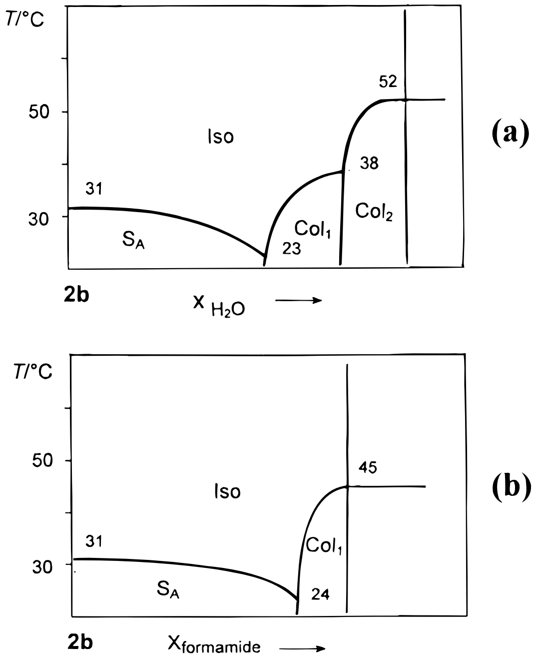

Figure 7. Simplified principal phase diagrams of compound **2b** (a) with water and (b) with formamide (Col$_1$ = columnar mesophase with spherulitic texture and Col$_2$ = columnar mesophase with mosaic texture).[8]

B. Oligo(oxyethylene) Derivatives with a Single Terminal Hydroxy Group. The tris(ethylene glycol) ether **2a** with only one hydroxy group exhibits exclusively a thermotropic S$_A$ phase which is slightly stabilized by addition of water (T_{cl} = 55 °C). No columnar phase was detected on cooling the water-saturated sample. However, the corresponding tetrakis(ethylene glycol) derivative **2b** forms two different columnar phases on addition of water. The principal phase diagram is shown in Figure 7a.

The columnar phase which occurs at lower water content displays a spherulitic and the other phase a mosaic-like texture. This phase sequence resemble that found for the diol **1c**/water systems. The main difference between the two phase diagrams is that the Col$_1$ phase still exists in the pure diol compound **1c** whereas it is induced in the monohydroxy compound **2b**. Only one columnar phase with a spherulitic texture (Col$_1$) is found on addition of formamide to **2b** (Figure 7b). This is contrary to the observations made with the diols **1b**−**d**. Here, the lyotropic systems with formamide have a larger number of columnar phases.

C. Lyotropic Properties in the Presence of *n*-Dodecane. In addition, the behavior of the amphiphiles was investigated with respect to the phase behavior in the presence of the lipophilic solvent *n*-dodecane. Most compounds are easily soluble in this hydrocarbon and their liquid crystalline phases are suppressed. The diols **1c**,**d** are only weakly soluble in

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(8) Most probably the phases Col$_1$, Col$_2$, and Col$_3$ also represent rectangular columnar mesophases.

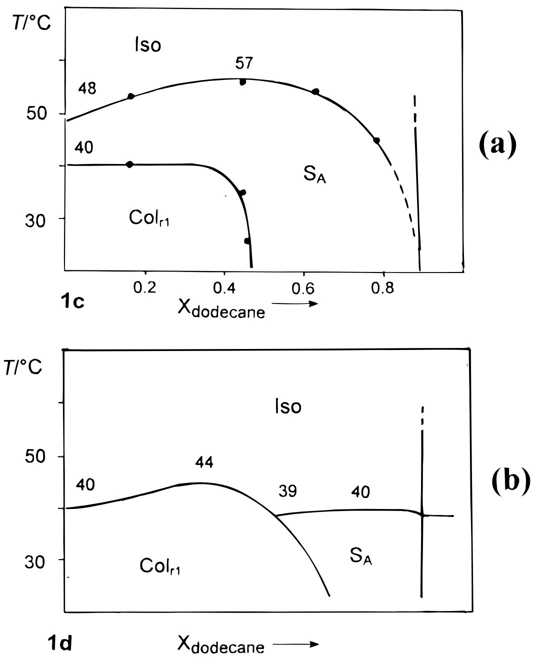

Figure 8. Simplified phase diagrams of compounds **1c**,**d** with dodecane.[6]

dodecane due to their rather large hydrophilic groups. These binary systems were investigated in more detail. The principal phase diagrams of **1c**,**d** with dodecane are given in Figure 8. In the contact region of the bis(ethylene glycol) derivative **1c** and *n*-dodecane, the smectic A-phase is stabilized and the columnar mesophase is significantly destabilized. After reaching a nearly equimolar ratio no columnar phase can be detected at all (see Figure 8a).

The tris(ethylene glycol) derivative **1d** displays a slightly different behavior (see Figure 8b). With increasing the amount of *n*-dodecane, the columnar mesophase is at first stabilized. A further increase of the *n*-dodecane concentration causes however a decrease of the stability of this columnar phase and gives rise to the appearance of a smectic A phase. The smectic phase remains stable until saturation. It seems that in contrast to protic solvents which stabilize the columnar mesophases lipophilic solvents destabilize columnar mesophases in favor of lamellar phases.

Discussion

The facial amphiphiles described here represent a novel, very interesting class of amphotropic materials.[9] These molecules consist of three distinct and incompatible parts: a rigid central part, two flexible and lipophilic chains, and a flexible and hydrophilic unit are connected in these Y-shaped molecules.[10] The pure compounds can form smectic and two of them also columnar mesophases. Microsegregation[11] of the incompatible parts into segregated regions and the rigid rodlike shape of the *p*-terphenyl units are responsible for their self-organization. A ribbon model as described in the Introduction (Figure 1) was proposed for the thermotropic columnar phases of compounds **1c**,**d**.[3b] The ribbons can be regarded as fragments of a collapsed smectic layer structure, and their formation should be caused by the segregation of the hydrophilic regions of the lateral groups from the rigid and lipophilic terphenyl cores into separate regions. An increase of the polarity and of the size of the lateral polar groups should facilitate the segregation. This was achieved for the thermotropic mesophases of the series of compounds **1a**−**d** by the introduction of a growing number of oxyethylene units.[3b]

In this contribution we have shown, that the same effect can be realized by the addition of protic solvents which specifically interact with the polar groups. Up to three different rectangular columnar phases are apparent: Col$_{r1}$ with a spherulitic texture, the highly viscous Col$_{r2}$ phase with a mosaic texture, and Col$_{r3}$ again with a spherulitic texture. The order of their occurrence on increasing solvent concentration is always Col$_{r1}$−Col$_{r2}$−Col$_{r3}$. The number of columnar phases depends mainly on the length of the lateral hydrophilic groups and their ability to coordinate solvent molecules. Only a Col$_{r1}$ phase is found for molecules with a medium size of the hydrophilic group, whereas all three columnar phases can be found for molecules with long polyether chains which can take up larger amounts of solvent.

Surprisingly, the lattice parameters of the columnar mesophases in all investigated systems are of the same order of magnitude. Especially parameter *a* varies only a little (4.02−4.15 nm); larger differences are found for parameter *b* (3.18−3.7 nm).[7] The length of the molecules in their most extended conformation amounts to $L = 4.1$ nm (CPK models). Because the alkyl chains are molten in the columnar mesophases, the effective length of the molecules in the mesophases is decreased. For S$_A$ phases of different 4,4″-bis(decyloxy)terphenyl derivatives, *d* values between 3.13 and 3.5 nm have been reported and a value of $d = 3.9$ nm was found in the more ordered S$_E$ phase.[3a,12] Therefore, we assume that the thickness of the ribbons (which represent fragments of an S$_A$ phase) should be correlated with the parameter *b* as already proposed for the thermotropic Col$_r$ phases of **1c**,**d**.[3b] However, this requires that the lateral distance between the ribbons, which is represented by the parameter *a*, must remain constant, independent of the type of Col$_r$ phase and independent of the number of solvent molecules incorporated in the polar regions. This means that on addition of solvent molecules only the thickness of the ribbons grows.

Using eq 1 and assuming a density of $\rho = 1$ g cm^{-3}, it can be calculated that on the average 5.1 molecules of **1c** should be arranged in the cross section of the ribbons of the thermotropic Col$_{r1}$ phase with a height (h) of about 0.45 nm.[13]

$$n = abhN_A(M + mM_{H_2O})^{-1}\rho \qquad (1)$$

A value of 4.9 molecule was found for the Col$_{r2}$ phase of the water-saturated sample of **1c** with a water content of $m = 4$ molecules. For compound **1d**, the corresponding values are 4.5 for the thermotropic Col$_{r1}$ phase and 4.2 for the Col$_{r3}$ phase of the water-saturated sample ($m = 11$ molecules water). Obviously, the number of molecules **1** arranged on the average side by side in the cross sections of the ribbons remains constant on addition of water. Because both the lateral distance between the ribbons and the number of molecules in the ribbons do not change on addition of water, the lateral diameter of the polar

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(13) The value of 0.45 nm corresponds to the average lateral distance between the centers of the alkyl chains.

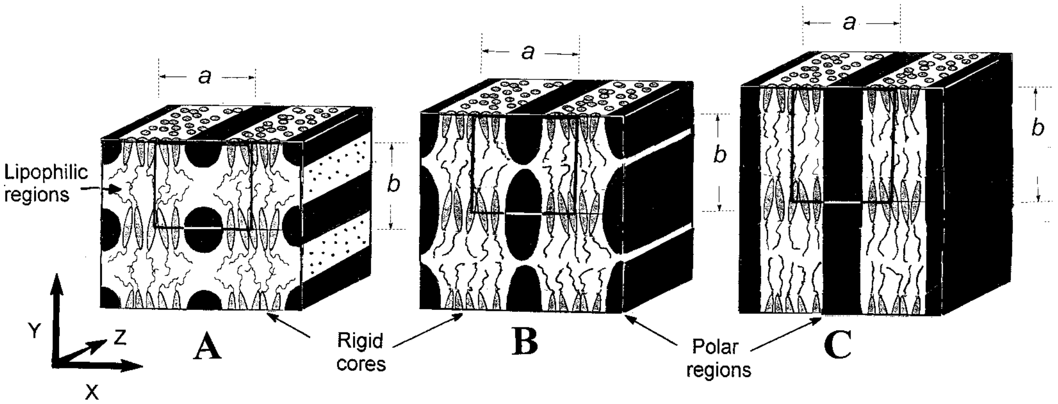

Figure 9. Cross sections through the three possible structures of the columnar mesophases of facial amphiphiles. The black areas represent the phase-separated polar regions consisting of the polar groups and the solvent molecules.

regions must remain constant. This means that the polar regions can only expand into the lipophilic layers of the alkyl chains. The consequence is that the lateral space available for the alkyl chains decreases on addition of protic solvents, the alkyl chains become more stretched, and the thickness of the ribbons increases. This would explain why only the lattice parameter *b* increases on addition of solvent molecules. Assuming this, there are three possible models for the lyotropic columnar mesophases which are shown in Figure 9. In case A the hydrophilic domains (black regions) do not exceed the length of the rigid units. The molten alkyl chains form layers in the *X*/*Z* plane, and the hydrophilic domains represent cylinders extended only in the *Z* direction. This model is the same as shown in Figure 1 for the thermotropic columnar phases of compounds **1c,d**. In case B the polar domains are extended in the *Y* direction and disturb the layers of the lipophilic chains. The thickness of the lipophilic layers becomes significantly smaller in the regions between the polar domains, i.e., the layers of the lipophilic region are strongly modulated. Probably, some neighboring polar domains can fuse providing randomly distributed linking points. Finally, in case C**,** the polar regions are completely fused in the *Y* direction and form layers in the *Y*/*Z* plane. The layers of the alkyl chains are patterned into cylinders extending only in the *Z* direction. Thus, in all three phases, the ribbons of the rigid cores remain unaffected and the rectangular 2D lattice is maintained. Only the shape of the lipophilic and polar regions and the space occupied by the different regions changes. We propose that the phases Col_{r1}, Col_{r2}, and Col_{r3} correspond to the arrangements A**,** B, and C, respectively. The strongly modulated lipophilic layers and the possibility of cross-links in the case of **B** can explain the high viscosity found in the Col_{r2} phase. According to this model, the type of columnar mesophase largely depends on the volume of the polar regions, consisting of the polar groups and the coordinated solvent molecules. The lateral groups of the diols **1a,b** and compound **2a,** for example, can coordinate only a small number of water molecules. The size and the polarity of the polar regions cannot reach the critical value which is necessary for their segregation from the rigid cores. Therefore, exclusively S_A phases are found. In compound **1c**, the larger and more polar lateral group itself is able to segregate and a thermotropic Col_{r1} phase is formed. Addition of water further increases the size of the polar regions, and the Col_{r2} phase is found. Because of the increased size of the hydrophilic group of **1d** in comparison to **1c**, less water is necessary to obtain the Col_{r2} phase. Additionally, a much larger number of water molecules can be coordinated to this group and at higher water content the Col_{r3} phase is obtained. Thus, the proposed model explains the observed order of mesophases and all other experimental findings.

With formamide as solvent the appearance of the columnar phases is often shifted to molecules with smaller polar groups, i.e., the Col_1 phase can be induced in compound **1b** and Col_{r3} is already found for **1c**.[8] Probably formamide can coordinate slightly better with the diol groups, or due to its larger size, fewer solvent molecules are necessary to get the same volume of the polar regions.

According to this model the columnar phases represent ribbon phases (modulated smectic phases).[14] Remarkably the ribbons are arranged in *simple* rectangular lattices in contrast to most other ribbon phases which form oblique or centered rectangular lattices. This special arrangement is provided by the topology of the connection of the polar groups with the rigid cores in central positions. The hydrogen bondings in the polar regions provide the strongest attractive force. Because they are located at both lateral sides of the ribbons, they keep them in a side-by-side arrangement, providing the simple rectangular lattice.

The lipophilic solvent *n*-dodecane should specifically interact with the lipophilic parts of the facial amphiphiles. On addition of this solvent the columnar phases are destabilized and replaced by smectic A phases. Also this observation is consistent with our model of the columnar mesophases. The lipophilic dodecane molecules should be mainly built into the sublayers of the lipophilic alkyl chains. A small number of them may contribute to a better space filling in the lipophilic region. Therefore the columnar phases can tolerate a certain amount of dodecane. If the polar groups are large as for example in compound **1d**, it is also possible that the columnar phases are slightly stabilized.

On further increasing the dodecane concentration, however, the lateral distances between the rigid cores are further enlarged. The result is that free space becomes available between the rigid cores. The lateral groups are able to fill up the space and get homogeneously distributed between the terphenyl cores. Thus, the segregation of the hydrophilic domains from the aromatic rigid cores is lost and only the segregation of these combined polar/rigid regions from the aliphatic regions remains. Thus, a smectic layer structure is found which is stabilized by hydrogen bonding between the polar groups distributed within the layers (see S_A phase shown in Figure 1).

Conclusions

The molecules discussed in this contribution combine typical features of three different types of mesophase-forming mol-

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ecules: the anisometric (specifically calamitic) mesogens, the amphiphilic molecules, and the block copolymers.[15]

In contrast to classical amphiphiles, which are well investigated, these new molecules can provide unusual novel supermolecular structures. Thus, the smectic phases of these amphiphiles represent monolayer structures in contrast to the double-layer lamellar mesophases of classical amphiphiles. Furthermore, different rectangular columnar phases have been found in dependence on the solvent concentration instead of hexagonal columnar phases which are predominately observed for lyotropic systems of flexible amphiphiles.

As in block copolymers and amphiphiles, microsegregation of chemically different molecular parts in different regions is a main driving force for the formation of their special supermolecular structures. Furthermore, their mesomorphic properties can be influenced by molecules, which specifically interact with one of the distinct molecular parts. However, the anisometry of the rigid cores provides a preferred parallel arrangement of the rigid units. This combination of rigidity and incompatibility and the special topology of the connection of the rigid and flexible molecular parts gives rise to an anisotropic swelling of the polar regions and thus provides the unique properties of these novel block molecules.[11,16]

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