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[17] Best results were obtained when the diamine and the carbonyl compound were mixed in dichloromethane at room temperature without an acid catalyst. The formation of the products was monitored by ^{1}H and ^{13}C NMR spectroscopy.
[18] Other Cu^{II} salts such as $Cu(SbF_6)_2$, $Cu(BF_4)_2$, $Cu(ClO_4)_2$, $Cu(OAc)_2$, $Cu(PF_4)_2$ showed lower selectivity in this reaction.
[19] The *ee* value of **9** was determined by chiral GC-MS on a Crompack Chirasil-DEX CB column.
[20] No epimerization of **9** was observed after treatment with acid.
[21] The absolute configuration of the newly formed stereogenic center of **9** was found to be *R* in each case when the (1*R*,2*R*)-diphenylethylene diamine ligand was used. The absolute configuration was determined by comparison of the optical rotation of **9** with the literature value.[15c]
[22] The ligand was prepared by condensation of benzaldehyde (2 equiv) with **1a** followed by addition of $Cu(OTf)_2$ (1 equiv).
[23] The reaction was quenched at $-72\,^{\circ}C$ by using trifluoroacetic acid and was allowed to stir at $-10\,^{\circ}C$ for 1 h. This workup procedure allowed the isolation of the HDA and aldol products. No interconversion between the aldol and HDA products was observed under these conditions.

A Thermotropic Mesophase Comprised of Closed Micellar Aggregates of the Normal Type**

Petra Fuchs, Carsten Tschierske,* Klaus Raith, Kumar Das, and Siegmar Diele

The ability of amphiphilic molecules to self-organize in aqueous systems with formation of micelles, vesicles, and lyotropic mesophases is of great importance for numerous applications of surfactants in several fields of science and technology, and it is also a prerequisite for the development of biological structures.[1, 2] In these polymolecular assemblies the hydrophilic parts (together with the solvent molecules) and the lipophilic parts of the amphiphiles are segregated into nanoscopic compartments, whereby changing the degree of curvature of the interfaces between the incompatible nanophases gives rise to a sequence of different mesophase morphologies. Hence, in dependence on the amphiphile structure, its concentration, and the temperature, different lyotropic mesophases can result.[1–3] Arrays of alternating layers yield smectic phases (SmA), regular arrangements of cylinders give rise to hexagonal columnar phases (Col_h), and closed globular or nonglobular micelles can form cubic mesophases (micellar cubic phases, Cub_I). Another type of cubic mesophase, consisting of two mutually interwoven networks of branched cylinders (bicontinuous cubic mesophases, Cub_V), occurs at the transition between smectic and columnar organization (Figure 1). For each of the nonlamellar mesophases two different types are possible. In normal phases (type 1, positive curvature of the polar/apolar interface), the stronger cohesive forces (hydrogen bonds) are located in the continuum surrounding the aggregates. In the reversed (or inverse) phases (type 2, negative interface curvature) they are

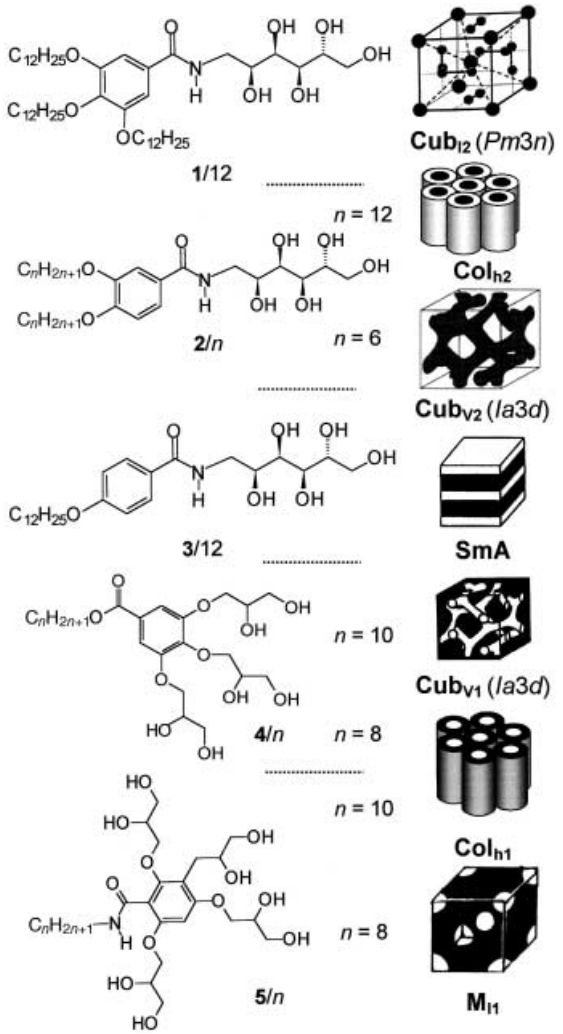

Figure 1. Dependence of the mesophase morphology of different polyhydroxy amphiphiles on the molecular structure. Abbreviations: Cub_{I2} = reversed discontinuous (micellar) cubic mesophase with *Pm3n* lattice; Col_{h2} = reversed hexagonal columnar mesophase; Cub_{V2} = reversed bicontinuous cubic mesophase with *Ia3d* lattice; SmA = smectic A-phase; Cub_{V1} = normal-type bicontinuous cubic mesophase with *Ia3d* lattice; Col_{h1} = normal-type hexagonal columnar mesophase; M_{I1} = mesophase comprised of discrete direct micelles with unknown lattice (the *Im3m* lattice is shown as one of the possible structures).

[*] Prof. Dr. C. Tschierske, Dr. P. Fuchs
Institute of Organic Chemistry
Martin-Luther-University Halle – Wittenberg
Kurt-Mothes-Straße 2, 06120 Halle (Germany)
Fax: (+49) 345-55-27223
E-mail: tschierske@chemie.uni-halle.de
Dr. S. Diele, Dr. K. Das
Institute of Physical Chemistry
Martin-Luther-University Halle – Wittenberg
Mühlpforte 1, 06120 Halle (Germany)
Fax: (+49) 345-55-27157
Dr. K. Raith
Faculty of Pharmacy
Martin-Luther-University Halle – Wittenberg (Germany)
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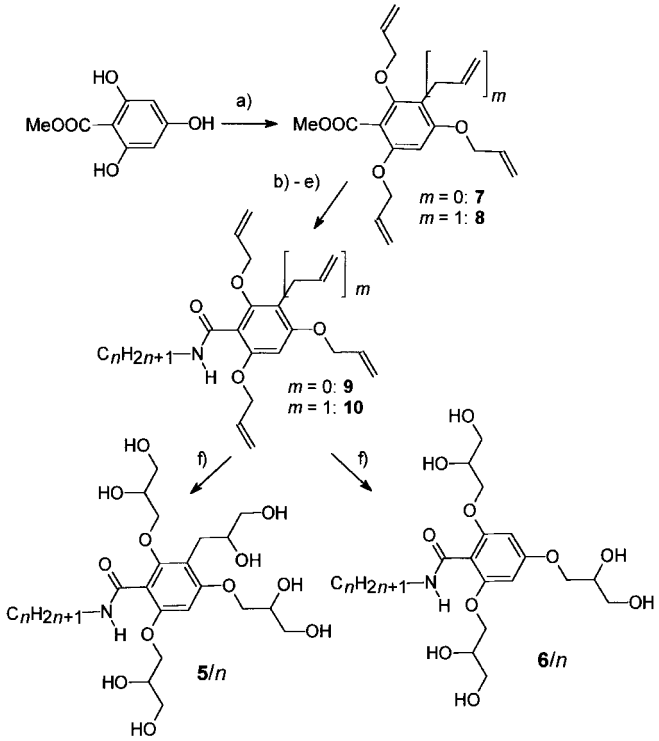
located inside the aggregates. The same phase sequence was found for binary AB diblock copolymers, which can be regarded as high molecular weight relatives of surfactants. Here, the phase sequence depends on the volume fractions of the two chemically connected, but incompatible polymer blocks.[4]

To confirm the generality of this sequence of distinct morphologies, it was a challenge to realize the same phase sequence in a series of low molecular weight amphiphiles in the absence of any solvent. Polyhydroxy amphiphiles are especially useful for this purpose, because they allow the precise control of the mesophase morphology by adjusting the molecular shape, the polar/apolar parity, and the attractive forces (hydrogen bonding), simply by changing the number and position of the alkyl chains and hydroxy groups.[5–9] Previously, all reversed-type mesophases (**1**–**3** in Figure 1),[7] as well as the normal-type bicontinuous cubic (Cub_{V1}) phase and the normal-type hexagonal columnar (Col_{h1}) mesophase (compounds **4**),[9] were realized with these materials. Now we have successfully completed this series, and here we report a novel thermotropic mesophase comprised of normal-type discrete micelles.

To achieve such a phase structure we synthesized compounds **6**/*n* and **5**/*n*, in which, respectively, three and four propane-2,3-diol units are attached to an aromatic linking unit such that the hydroxy groups can completely surround the aromatic core. These compounds were obtained as shown in Scheme 1. The allylation[10] of methyl 2,4,6-trihydroxybenzoate led to a 3:1 mixture of the tris(allyl ether) **7** and the product of additional *C*-allylation[11] (**8**). These were separated by chromatography and transformed into the final compounds **5**/*n* and **6**/*n* as shown in Scheme 1.[12–14]



Scheme 1. Synthesis of compounds **5**/*n* and **6**/*n*. a) $BrCH_2CH{=}CH_2$, K_2CO_3, DMF, 100 °C, 10 h; b) chromatographic separation of **7** and **8**; c) NaOH, DMSO, H_2O, 60 °C, 6 h;[12] d) HOC_6F_5, dicyclohexylcarbodiimide, THF, 25 °C, 14 h;[13] e) $C_nH_{2n+1}NH_2$, CH_2Cl_2, 25 °C, 12 h; f) *N*-methylmorpholine *N*-oxide, cat. OsO_4, acetone, H_2O, 25 °C, 48 h.[14]

The obtained compounds (see Table 1)[15, 16] were first investigated by polarizing microscopy and differential scanning calorimetry (DSC). No mesophase could be detected for **6**/8, whereas a spherulitic texture, as is typical for hexagonal columnar phases, was observed after supercooling a melt of **6**/10. Compound **5**/10 with four diol groups shows an enantiotropic (thermodynamically stable) hexagonal columnar mesophase. X-ray scattering confirmed this phase assignment (diffuse wide-angle scattering and three sharp reflections in the small-angle region, the positions of which correspond to $1:3^{1/2}:5^{1/2}$; $a_{hex} = 3.87$ nm at $T = 100$ °C). The diameter of the columns (3.87 nm)[17] is in good agreement with an organization of the strongly coiled fluid alkyl chains in cylinders with a surrounding corona of hydrogen-bonding networks (Col_{h1}, see Figure 2).[18] Compound **5**/9, which is one CH_2 unit shorter than **5**/10, also forms a columnar phase, but with significantly lower mesophase stability.

Table 1. Transition temperatures T [°C] and corresponding enthalpy values ΔH [kJ mol^{-1}] (lower lines) of **5**/*n* and **6**/*n*.[a]

Comp.	T [°C] ΔH [kJ mol^{-1}]
5/8	Cr 84 (M_{I1} 55) Iso
	22.4 0.8
5/9	Cr 91 (Col_{h1} 80) Iso
	43.1 1.1
5/10	Cr 86 Col_{h1} 118 Iso
	20.2 1.1
6/8	Cr 99 Iso
	48.0
6/10	Cr 109 (Col_{h1} 95) Iso
	44.6 0.8

[a] Abbreviations: Cr = crystalline solid state; Iso = isotropic liquid phase; for the other abbreviations, see Figure 1. Transition temperatures and enthalpies were determined by DSC (Perkin-Elmer DSC-7, first heating scan, rate: 10 K min^{-1}) and confirmed by polarizing optical microscopy. Values in parentheses refer to monotropic (metastable phases), which were determined in the second heating scan.

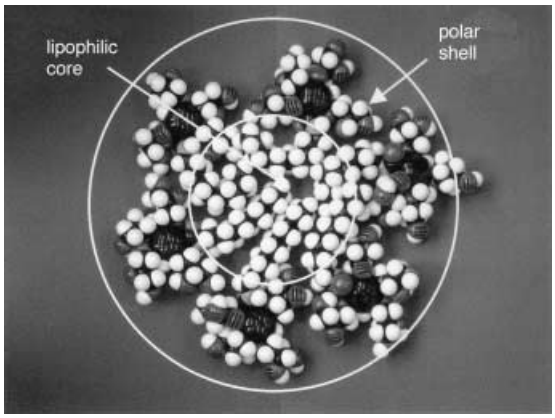


Figure 2. Cross section through a column of the Col_{h1} phase of **5**/10. A related picture would be found for the cross section through spherical micelles of the M_{I1} phase of **5**/8.

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Compound **5**/8 behaves quite differently. The first DSC heating scan shows only a broad endotherm with a maximum at 84 °C which corresponds to a melting process. On cooling at 2 K min^{-1} an exotherm with a rather small enthalpy ($\Delta H = -0.8$ kJ mol^{-1}) can be found at 33 °C followed by a glass transition at 15 °C. In the second heating scan, after the glass transition at 18 °C, an endotherm with equal enthalpy to the phase transition in the cooling scan is found at 55 °C (see Figure 3). Investigation by polarized light microscopy reveals

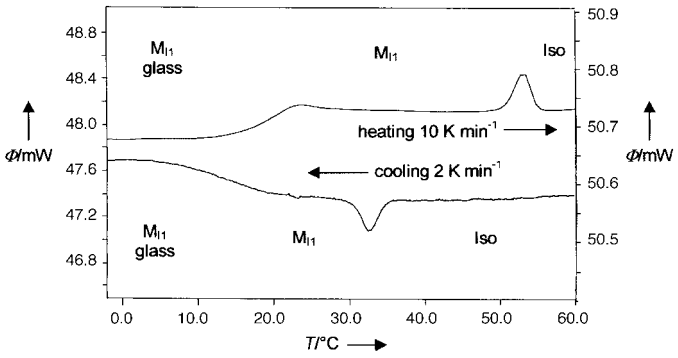

Figure 3. DSC heating (second heating scan) and cooling scan of compound **5**/8. The heat flow Φ on the left-hand side corresponds to the heating scan, and that on the right-hand side to the cooling scan; for abbreviations, see Figure 1.

that on cooling the isotropic liquid phase becomes rather viscous at 30–35 °C. On heating, the viscosity decreases at about 50–55 °C. These observations indicate the presence of an optically isotropic mesophase (M) which undergoes a transition to the liquid state at circa 55 °C and vitrifies slightly below room temperature. Although this mesophase is only monotropic (metastable), crystallization occurs only after prolonged storage (several days) above the glass transition temperature. Not only the crystallization, but also the transition from the liquid state to this mesophase can be significantly supercooled; this is typical for cubic mesophases and points to the presence of a three-dimensional lattice within this mesophase.

To obtain further information on the structure of this mesophase we investigated the contact region of **5**/8 with **4**/10, for which a type 1 bicontinuous cubic mesophase (Cr 75 Cub_{V1} 108 Iso, see Figure 1) was confirmed in earlier work.[9b] In the contact region between these two compounds a concentration gradient develops. A birefringent mesophase with a spherulitic texture typical of hexagonal columnar phases is induced between < 20 °C and 96 °C, and separates the mesophase of **5**/8 and the Cub_{V1} phase of **4**/10 (see Figure 4). The replacement of the type 1 bicontinuous cubic phase of **4**/10 by a columnar mesophase (Col_{h1}) indicates that the polar/apolar interface curvature becomes more positive with increasing concentration of **5**/8.[19] This means that in the isotropic mesophase of **5**/8 the polar/apolar interface should be more strongly curved than in the columnar phase, and this confirms that the mesophase of **5**/8 is composed of discrete type 1 micellar aggregates (M_{I1}). These spheroidal aggregates comprise the alkyl chains surrounded by the polar parts of the molecules, which form a continuous hydrogen-bonding network around

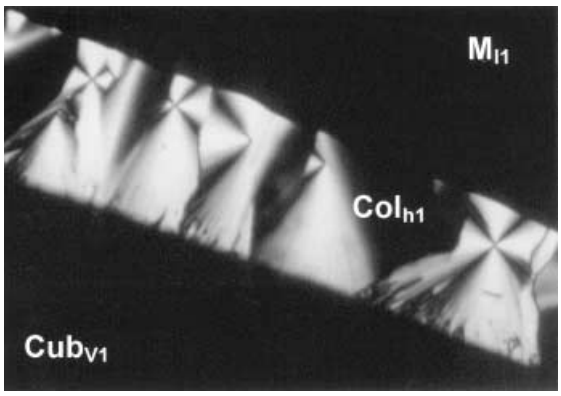

Figure 4. Hexagonal columnar phase developing in the contact region between the bicontinuous cubic phase of **4**/10 (Cub_{V1}) and the isotropic mesophase of **5**/8 (M_{I1}), as observed between crossed polarizers at 50 °C.

them. X-ray scattering investigations, performed with a Guinier film camera and a goniometer, should provide information about the organization of these micelles in the optically isotropic mesophase of **5**/8. A diffuse scattering in the wide-angle region (maximum at $d = 0.42$ nm) confirms the liquidlike disordered state of the alkyl chains and the hydrogen bonding networks. In the small-angle region, rather diffuse scattering can also be found, but sometimes three sharp nonequidistant reflections, corresponding to $\theta_1 = 1.57°$, $\theta_2 = 2.72°$ and $\theta_3 = 4.07°$ can be observed instead (see Figure 5). The positions of these sharp reflections and their

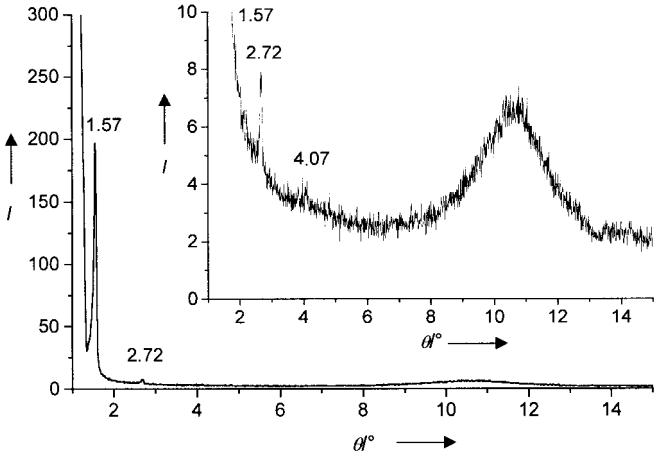

Figure 5. X-ray diffraction pattern of the M_{I1} phase of **5**/8 at 40 °C.

relative intensities are quite distinct from the three most intensive reflections typically found in the diffraction pattern of the *Pm*3*n* lattice which is most often observed for micellar cubic phases of type 1 lyotropic systems and for the thermotropic type 2 micellar cubic mesophases of polyhydroxy amphiphiles **1**/*n*[7b–d] and dendritic molecules.[20] Instead, an assignment of these reflections is possible on the basis of a hexagonal lattice (*hk* = 01, 11, 21). However, a hexagonal arrangement of columns can be excluded because of the optical isotropy of this mesophase and the results of the miscibility studies. Therefore, we can assume a close cubic packing (*Fm*3*m* or *Im*3*m*) or a three-dimensional hexagonal

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packing of spherical micelles ($P6_3/mmc$),[21] but the small number of reflections did not allow a certain assignment to one of these possibilities. As mentioned above, the occurrence of a superstructure in the M_{II} phase is highly sensitive to the experimental conditions and can only occasionally be found in the X-ray diffraction experiments. It is often distorted, so that in most cases only a short-range ordered structure, characterized by a rather diffuse primary peak and its higher order was recorded.[22] This micellar mesophase can be frozen into the glassy state to furnish a (ordered or disordered) micellar glass phase below 18 °C.

In summary, a novel thermotropic mesophase, comprised of normal-type micellar aggregates has been obtained for the first time for a low molecular weight amphiphile in the absence of water or any other solvent. Thus, all main aggregate types known from aqueous lyotropic systems have successfully been realized as their thermotropic analogues within a single series of structurally related amphiphiles (**1**–**5**, see Figure 1). These investigations confirm that water is not necessary for the occurrence of any of the aggregate morphologies known from aqueous systems. However, because of the unique combination of organizing forces and mobility in liquid water, it can significantly increase the number of low molecular weight amphiphiles capable of forming organized soft matter.

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[15] The final compounds were purified by repeated column chromatography on reverse-phase silica gel (LiChroprep RP-18, 40–63 mm, Merck). All analytical data are in accordance with the proposed structures, for example, *N*-octyl-2,4,6-tris(2,3-dihydroxypropoxy)-3-(2,3-dihydroxypropyl)benzamide **5**/8: ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ 0.82–0.88 (m, 3H, CH_3), 1.20–1.34 (m, 10H, CH_2), 1.39–1.55 (m, 2H, CH_2), 2.58–2.70 (m, 2H, $ArCH_2$), 3.06–4.12 (20H, NCH_2, CH_2OH, $CHOH$, OCH_2) 4.27–4.34 (m, 1H, OH), 4.37–4.58 (m, 3H, OH), 4.59–4.69 (m, 1H, OH), 4.80–4.89 (m, 2H, OH), 4.91–4.97 (m, 1H, OH), 6.43 (s, 1H, ArH), 7.98 (t, 1H, NH); ^{13}C NMR (400 MHz, CD_3OD): δ = 168.00 (CO), 159.69, 159.64, 156.33, 114.19, 113.55 (C-Ar), 94.13 (CH-Ar), 72.50, 71.56, 71.49, 70.88, 70.82, 70.78 (CH), 75.84, 75,70, 70.71, 70.13, 70.04, 65.82, 63.23, 63.15 (OCH_2), 40.26 (NCH_2), 32.16, 29.58, 29.53, 29.44, 27.43, 27.38, 22.84 (CH_2), 13.59 (CH_3); EI-MS, *m*/*z* (%): 577 [M^+] (0.14), 546 (6), 528 (2), 516 (4), 503 (7), 486 (7), 472 (33), 454 (31), 442 (60), 368 (30), 313 (53), 239 (50) 165 (100); positive HR-ESI-MS (Q-TOF 2 instrument; Micromass, Manchester UK): found: 600.3005 [M+Na]$^+$; calcd for $C_{27}H_{47}NO_{12}Na$: [M+Na]$^+$ 600.2996.

[16] All compounds **4**–**6** are complex mixtures of diastereomers. This structural diversity is in our case helpful, because it inhibits the rapid crystallization of the samples and therefore allows detection of the mesophases.

[17] The molecular length amounts to $L = 2.5$ nm in the most extended conformation.

[18] About six molecules are arranged on average in the cross section of a 0.45 nm thick section of the columns, which was calculated according to equation (1), wherein $\rho = 1\ g\,cm^{-3}$, N_A = Avogadro number, M = molecular mass, and $h = 0.45$ nm (which corresponds to the position of the maximum of the diffuse scattering in the wide-angle region of the X-ray pattern).

$$n = a_{hex}^2/2\sqrt{3}h\,(N_A/M\rho) \quad (1)$$

[19] If the interface curvature became less positive, induction of an SmA phase could be expected.[7, 9]

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