Long-Lived Micellar *N*-Alkylaldonamide Fiber Gels. Solid-State NMR and Electron Microscopic Studies

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Abstract: Aqueous geis containing 1% of *N*-octylgluconamide usually crystallize within a few hours. They remain stable for more than 2 months if 0.1–0.4% of sodium dodecylsulfate (SDS) is added. It was shown by ^2H NMR spectroscopy and electron microscopy that the gels contained fibers of bimolecular thickness (4 nm) and several micrometers lengths in equilibrium with micelles. Relatively high concentrations of micelles extended the gel's lifetime, presumably because the micelles dissolved the head-to-tail sheets of crystallization nuclei too rapidly to allow crystal growth. At temperatures below the gelation point the micelles are as unfit solvents for magnesium octaethylporphyrin as the fibers themselves and show immobile oligomethylene chains in ^1H NMR solution spectra. Comparisons with the diastereomeric gulon- and mannonamide molecular bilayer sheets indicate that the gluconamide rods with the highest curvature contain the least mobile core. Water-insoluble *N*-octadecylmannonamide precipitates from micellar solutions either in the form of a statistical mixture of P- and M-helices or as pure M-helices depending on added detergent and time. The results determine two rules for syntheses of organized systems based on micellar fibers: guest molecules must be tailored in order to fit into the amide hydrogen-bonded fibers and micelles, and the fibers must be chiral and kept in a medium that dissolves crystallization nuclei.

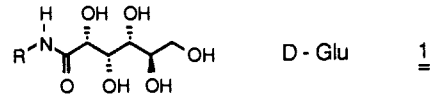
The amphiphilic *N*-octyl-D-gluconamide (**1a**) is practically insoluble in water at room temperature, dissolves readily in hot water (≈500 g/L at 85 °C) and forms ultrathin micellar fibers[1-3] (diameter, 4 nm; lengths, several μm) on cooling. These fiber aggregates are produced by very rapid and cooperative formations of linear hydrogen bond chains between the secondary amide groups.[4] This process may be considered as a model for the preformation of hydrophobic protein fibers in aqueous media. They must not be confused with rodlike micelles which are simply enforced by high concentrations (~30%). These worm-like chains are very flexible and have a persistence length of only about 50 nm corresponding to a poor length-to-diameter ratio of 10. The fiber micelles discussed here exist at much lower concentrations (~0.5%) and, more important, they show length-to-diameter ratios in the order of 10^4. This leads to clear separation of individual fibers by large water volumes and makes them useful starting materials for the construction of complex reaction systems. A very helpful detail is the proven fact that some mixed systems made of two diastereomeric amphiphiles clearly separate quantitatively into two discernible fibers.[6]

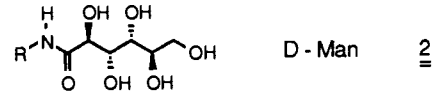
A major problem with the use of fibrous aggregates was their limited lifetime and structural changes.[2,7] The originally clear or slightly opaque gels usually decomposed within a day, although the formation of crystals is retarded by the chiral bilayer effect, namely the rearrangement from tail-to-tail curved bilayers to head-to-tail planar crystal sheets.[1,8]

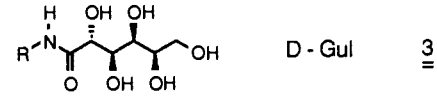
Short term stabilization was possible by coating the newly formed fibers with a phosphotungstate "glass" at pH = 7.[9] This technique yielded uniform preparations for electron microscopy[1] but had no significant effect on the gel's lifetime. Attempts to stabilize the ultrathin fibers by cross-linking with glutardialdehyde failed. In this paper we now describe conditions under which the ultrathin fibers undergo a continuous exchange of material with the bulk aqueous volume. The precipitation of crystals does not occur for at least 5 months and possibly not at all.

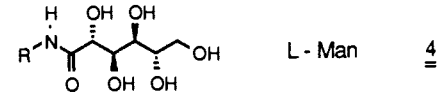
Results and Discussion

***N*-Octylglyconamide Micelles.** We selected three out of eight possible diastereomers, D-gluconamide (**1a**), D-mannonamide (**2a**), and D-gulonamide (**3a**), to evaluate the importance of stereochemical differences for fiber properties. Their aggregation behavior represents the typical variations: **1a** aggregates to form









a) R = CH_3 - $(CH_2)_6$ - CH_2 -

b) R = CH_3 - $(CH_2)_6$ - CD_2 -

c) R = CH_3 - $(CH_2)_{16}$ - CH_2 -

the most interesting helical rods with a diameter of 4 nm, **2a** gives molecular bilayer sheets which roll up to elongated, thick scrolls,[2] and **3a** directly precipitates from hot aqueous solution in crystalline form. All three compounds are practically insoluble in water at room temperature but dissolve at 90 °C: **1a** to 50% (w/v), **2a** to 3% (w/v), and **3a** to 100% (w/v). The racemate of D- and

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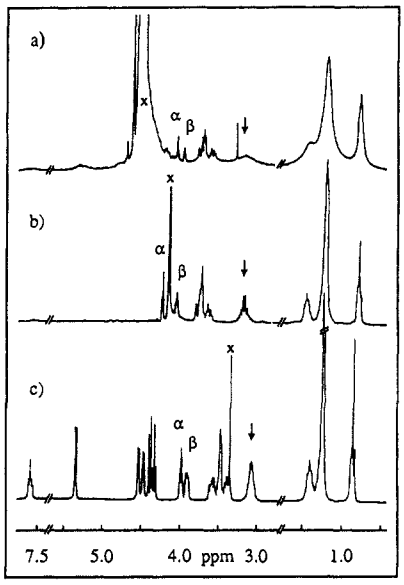

Figure 1. ^{1}H NMR spectra of gluconamide **1a** (a) 30 mg in 0.5 mL of D_2O + 2% phosphotungstate, pH = 7, 40 °C, 128 scans; (b) 80 °C, 32 scans, and (c) 20 mg in 0.3 mL of DMSO-d_6, 25 °C, 16 scans; extra signals are OH and NH. Arrow: CH_2 next to amide, × HDO signal.

L-*N*-octylgluconamide is less soluble by a factor of about three than the pure enantiomer.

Obviously, the large differences in solubilities are *not* related to the structure of the primary aggregates since planar crystal sheets and ultrathin rods are formed from diastereomers of similar solubility. The solubilities are, however, related to sterical interactions within the head groups: 1,3-*syn*-hydroxyl groups disturb the linear all-trans conformation and thereby enhance hydration. **1a** and **3a** are therefore more soluble than **2a** by an order of magnitude. **3a** is more soluble than **1a**, presumably because the disturbing hydroxyl interaction occurs only in **3a** directly on the hydrophilic surface of the crystals. Thus penetration of water into crystals of gulonamide **3a** should be facilitated.

In small micelles of high curvature the head groups should always be highly hydrated, independent of the applied micelle model.[10-13] One may therefore predict that in hot solutions all critical micellar concentrations (cmc) of the three diastereomers should be identical. This was verified by lipid concentration dependent fluorescence measurements of 1,6-diphenyl-1,3,5-hexatriene (DPH).[14] D- and L-gluconamides as well as their racemic mixture gave exactly the same cmc of 0.85% (27.7 mmol) at 80 °C. The cmc of mannonamide **2a** is somewhat higher (0.93%; 30.3 mmol; 90 °C) and that of gulonamide **3a** a little bit lower (0.80%; 26.0 mmol; 80 °C). Both deviations are barely out of the experimental error range and far from significance. Formations of micelles in solution and of solid precipitates are therefore unrelated aggregation processes.

NMR spectroscopy of the hot micellar solutions and of the micelles dissolved in the bulk water phase of the gel was used to characterize the aqueous phases. Spin patterns in ^{1}H NMR spectra of gluconamide **1a** are the same in monomolecular DMSO-d_6 solutions at room temperature and in aqueous micellar solutions at 80 °C (Figure 1b,c). Most significant is the multiplet for the methylene group bound to the amide nitrogen atom at δ = 3.08 ppm. The signal's sharpness clearly indicate that the amide group is not involved in hydrogen bonds. If the solution is cooled below the gelations point, this signal is broadened up and no splitting remains (Figure 1a). Furthermore the signals of the protons of the hydrocarbon chains broaden, whereas the head group signals lost intensity in the gels but did not change their splittings. Thus it is evident that in the micelles below the gel's melting point the mobility of the oligomethylene chains is greatly reduced. Another interesting variation occurs in the chemical shifts of the methine protons next to the carboxamide group: on cooling the α-CH proton signal shifts upfield by 0.16 ppm, the β-CH proton by 0.06 ppm. All these effects point to the formation of strong amide hydrogen bonds, which causes immobilization as well as loss of electron density in the environment of the carbonyl groups.

NMR spectra of mannonamide **2a** also show the upfield shift of the α-CH proton signal, but the corresponding signal of gulonamide **3a** does not change. We conclude that the disturbances of the head group linearity in **3a** prevent the formation of amide hydrogen bonds within the micelles.

***N*-Octylglyconamide Fibers.** The self-organization within the micelles and, possibly, their assembly to fibers can be followed by differential scanning calorimetry. Glucon- and mannonamides (**1a** and **2a**) show sharp gelation points at 75 °C and 99 °C. This is presumably caused by the cooperative formation of amide hydrogen bond chains. The gulonamide **3a** also gave an exothermic peak at the solidification point, but the temperatures were not reproducible. Three independent measurements of the solidification curve gave peaks at 28 °C, 13 °C, and 3 °C. Solidification of gulonamide seems not to be triggered by a cooperative molecular interaction but by statistical appearances of crystallization nuclei. Melting, on the other hand, always occurs at 55 °C. This difference between the aggregation behavior of the diastereomers again confirms that glucon- and mannonamides form tighter, probably hydrogen-bonded aggregates than gulonamide.

At high temperatures, the micelles of all three compounds should be equally good solvents for hydrophobic guest molecules. We proved this consideration with magnesium octaethylporphyrin (MgOEP). Indeed it was found that MgOEP dissolved well in hot micellar solution but rapidly precipitated on cooling. Differences between the hydrogen-bonded gel aggregates of **1a** and **2a** and the crystals of **3a** were not observable. Possibly the porphyrin molecules are too voluminous to fit into the disturbed gulonamide crystals.

Due to technical limitations of the ^{1}H liquid state NMR spectrometer only contributions from the micellar part of the system fiber-micelle were detectable. For more detailed studies of this equilibrium and the influence of head group stereochemistry on the membrane mobility ^{2}H NMR solid-state echo spectra were recorded, showing strong, anisotropic quadrupolar couplings. Advantages of ^{2}H NMR spectroscopy are the following: (i) the purely intramolecular interaction of the deuteron quadrupolar moment with the electric field gradient (EFG) of the C-^{2}H bond leads to well-resolved solid-state spectra, which can be related to the type of motional orientation of the C-^{2}H bond, (ii) and by labeling special segments of a molecule, localized molecular motions can be monitored separately without disturbance by other hydrogens.

The α-methylene group neighboring to carboxamide was deuterated, because this segment was shown to be most sensitive to conformational changes induced by variations of the head group stereochemistry (see above). ^{2}H NMR spectra of the glyconamides-d_2 **1b**, **2b**, and **3b** were recorded in deuterium-depleted water containing 2% of phosphotungstate. The spectra possess sufficient intensity, although the amide concentrations of the NMR samples were comparatively low.

In hot aqueous solution (>70 °C) the deuterium signal of gluconamide **1b** appears as a singlet (Figure 2). On cooling to 7 °C gelation occurs, and the singlet is replaced by a Pake powder spectrum with a quadrupole splitting of 118 ± 2 kHz, corresponding to a quadrupolar coupling constant of 157 ± 3 kHz. This represents typical values of immobile methylene groups in solid material,[15-17] where immobility is defined with respect to the

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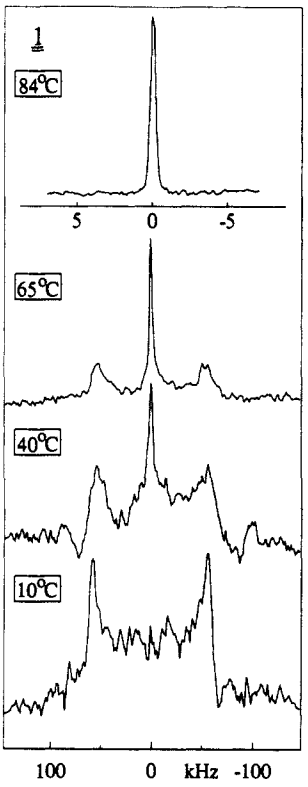

Figure 2. ^2H NMR spectra of **1b** (60 mg in 0.2 mL of deuterium-depleted H_2O + 2% phosphotungstate, pH = 7, 46.07 MHz, 1000 scans). The spectra show the temperature dependent phase equilibrium between the Pake powder pattern of solid gel fibers and the singlet of micelles (quadrupole splitting 118 ± 2 kHz).

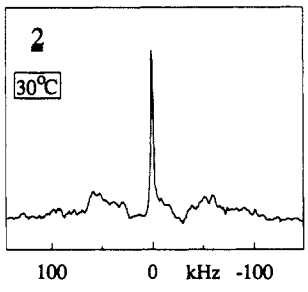

Figure 3. ^2H NMR spectrum of mannonamide **2b** (6 mg in 0.2 mL of H_2O, see Figure 1; 50 000 scans).

characteristic time scale of deuteron NMR (10^{-5} s). The outer edges of the powder pattern disappear in the noise. At 40 °C both signals, the Pake spectrum for an anisotropic solid and the singlet for an isotropic solution, are present. The intensity ratio is about 10:1. At 65 °C the macroscopic gel appearance remains unchanged, but the fraction of the solution signal rises to about 20%. The mobility of the CD_2 group within the solid fiber remains in the limit of slow motional exchange, while more material is transferred into the micellar solution. At 84 °C, clearly above the gel's melting point, again only the solution spectrum occurs. Concentration ratios at different temperatures, calculated from integrals of the powder pattern and the central signal, show that at e.g. 60 °C about 13% of micelles have been separated from the fibers.

Mannonamide **2b** is less soluble by a factor of about 15 as compared to the corresponding gluconamide **1b**.[3] This condition leads to ^2H NMR spectra with unfavorable signal-to-noise ratios. At 30 °C we obtained a spectrum, wherein the powder pattern as well as the singlet of the micelles are detectable (Figure 3). The splitting of the Pake spectrum amounts to 124 ± 2 kHz

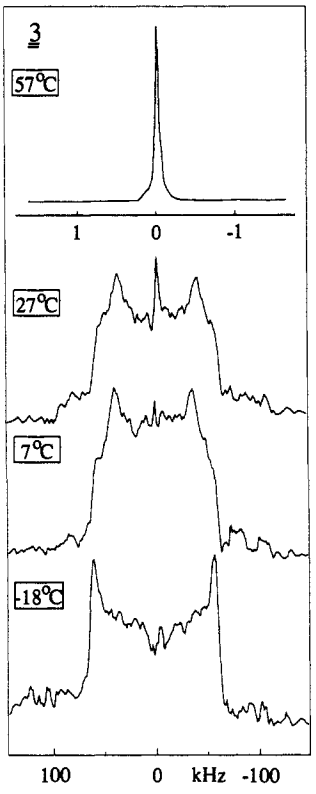

Figure 4. ^2H NMR spectra of gulonamide **3b** (60 mg in 0.2 mL of H_2O, see Figure 1; 1000 scans). Above −18 °C the signal of the solid crystals deviates from the typical powder pattern. See text and Figure 5.

(coupling constant 165 ± 3 kHz), again corresponding to immobile methylene groups. Obviously, the micelles of mannonamide **2b** also are in a phase equilibrium with solid gel fibers as observed for **1b**.

As mentioned above gulonamide **3b** is more water-soluble than the other amides and forms only noncurved platelets in the solid state. Since its stereochemistry is very similar to gluconamide this somewhat exotic carbohydrate derivative offers the possibility to compare hydrophobic bilayers which differ only in curvature. In the temperature range of −18 °C up to 50 °C the solid-state signal deviates from the typical powder pattern. The quadrupole splitting of the singularities amounts to 91 ± 2 kHz and the coupling constant to 121 ± 3 kHz. The center of the signal grows with increasing temperature, and shoulders appear at the outer wings of the singularities (Figure 4). Around 20 °C the singlet of the micelles occurs in addition to the broad signal, and above 50 °C all anisotropic contributions of the spectrum are lost, corresponding to the solid-to-liquid transition. In addition the spectra show the relative abundance of dissolved micelles. Up to 40 °C, close to the melting point, less than 10% of the material was in the dissolved state. All changes of the line shapes are fully reversible, independent of temperature variation by heating or cooling. To explain the deviation from the Pake spectrum, we assume a fast motional process with a symmetry lower than 3-fold, e.g., a two-site jump process. As a consequence, the motionally averaged EFG tensor is not symmetric anymore. An asymmetry parameter of $\eta = 0.24$ and a coupling constant of about 126 kHz can be estimated. In Figure 5 both spectra, the calculated and the experimental, are included indicating a reasonable fit. These results are consistent with the often discussed model of a two-site trans–gauche isomerization with unequal occupation probabilities for each site (P_t,P_g).[15,18,19] For gulonamide **3b** we estimate a population ratio of P_t:P_g = 0.83:0.17. Thus, in contrast to the fibrous, highly curved bilayers of gluconamide **1b**, the phase

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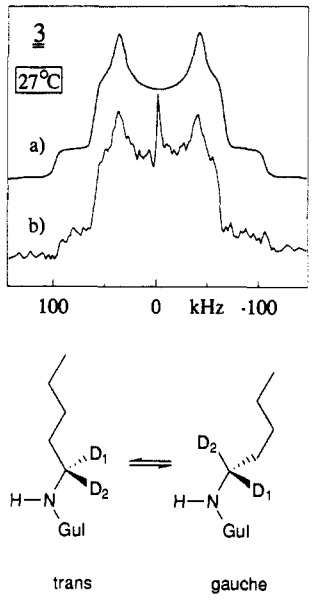

Figure 5. The calculated (a) and the experimental (b) solid-state spectra of **3b** with an asymmetry parameter of $\eta = 0.24$ show reasonable fit. See text. Note that in the gauche conformation D_1 occurs at the position originally occupied by D_2.

equilibrium of the planar bilayer of gulonamide **3b** is accompanied with a fast conformational change of deuterons next to the amide group, even at low temperatures.

A final hint on the different aggregation behavior of the three diastereomers comes from solid-state ^{13}C chemical shifts of the terminal methyl group in the alkyl chains. The signal in ^{13}C CP/MAS spectra appears at $\delta = 15.90$ ppm vs TMS in the crystalline precipitates of glucon- and gulonamides but at 14.40 ppm for the mannonamide. Since ^{13}C signals are shifted to higher δ values by more polar solvents in this order of magnitude,[20] we conclude that glucon- and gulonamides occur in head-to-tail sheets, whereas the least soluble mannonamide without 1,3-OH interaction may crystallize in tail-to-tail sheets.

The results of this section can be summed up as follows: the curved bilayer superstructures, namely rods and scrolls, contain tight hydrophobic cores and release small micelles, whereas the crystal-like planar sheets contain a more flexible hydrophobic core. Less micelles dissociate from planar bilayers than from the curved analogues (Figure 6).

Micelles and Fiber Longevity. From experience we know that micellar gluconamide fibers and the resulting gels are stable for several days at 60 °C, for several hours at room temperature, and for minutes at 5 °C. Since the NMR results have shown that a raise in temperature causes the formation of small micelles, we conclude that the presence of high concentration of micelles prevents crystallization. This is a reasonable conclusion, if one keeps in mind that crystallization is connected with a slow rearrangement from tail-to-tail micellar bilayers to head-to-tail crystalline sheets. The micelles may just dissolve the nuclei faster than they are able to grow to crystals.

To enhance the gel's lifetime, we added 10% of detergent (molar ratio 10:1), namely sodium dodecylsulfate (SDS), to the micellar gluconamide solution, and indeed we obtained indefinitely stable fibers and gels at 60 °C. These gels were slightly opaque and stayed clear for longer than a month. Electron microscopy of such a gel gave well-resolved micellar fibers (Figure 7b). In the absence of SDS, multihelical aggregates of unknown multiplicity are formed under the same conditions, and the gel crystallized quantitatively within 96 h at 60 °C. If this crystal suspension was cooled to room temperature, the micelles in the supernatant were sufficiently concentrated to form a gel again. At room temperature 40% of SDS (molar ratio 2.5:1) with respect to gluconamide was needed to stabilize the gel for more than 2

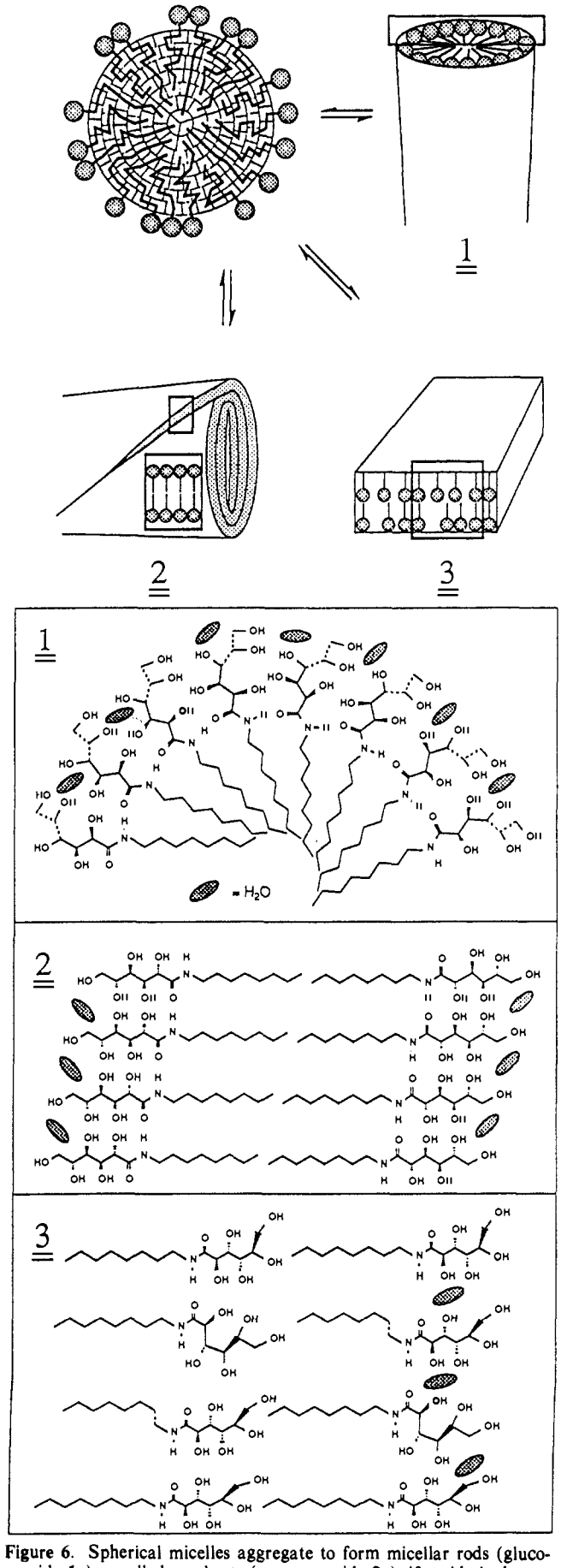

Figure 6. Spherical micelles aggregate to form micellar rods (gluconamide **1a**) or rolled-up sheets (mannonamide **2a**), if amide hydrogen bond chains are allowed by a regular head group conformation. The assumed irregularity of the gulonamide **3a** head groups leads to highly hydrated crystals.

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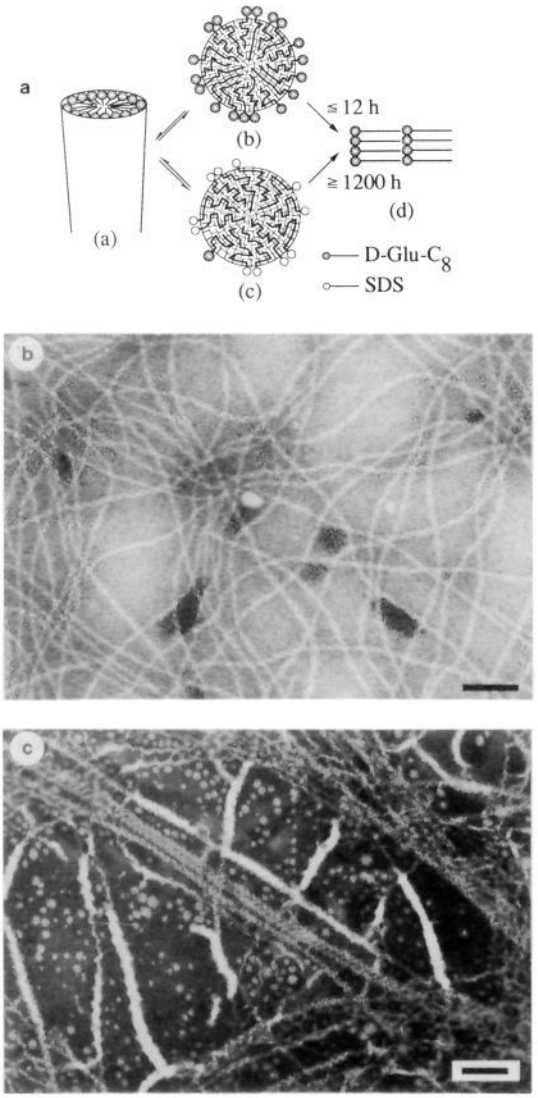

Figure 7. (a) In the presence of detergents, e.g., SDS, micellar fibers do *not* rearrange to crystals, because crystallization nuclei with head-to-tail sheets cannot be formed. (b) Electron micrograph of a 2-month old gluconamide **1a** gel, which was kept at 60 °C in the presence of SDS (molar ratio 10:1). Micelles and double helices occur (PTA 2% poststrained, bar = 100 nm). (c) Electron micrograph of a gel, which was kept at 20 °C and contained more SDS (molar ratio 2.5:1). Vesicles and multiple helices are apparent (PTA 2% poststained, bar = 100 nm).

months. These gels were white and showed thicker fibers (multihelical type) than the 60 °C gel (bulgy helices) in electron micrographs (Figure 7c).

The thermodynamical stability of the fiber structures with extremely high surface energies can only be understood, if the nonoccurrence of crystal can be explained. Below the gel melting points, however, SDS has practically no effect on the solubility of gluconamide crystals. In this temperature range SDS is obviously not able to penetrate into the amide hydrogen bond chains. Presumably only the slow formation of the primary head-to-tails (= enantiomer polar) sheets, which would act as nuclei, is impeded by SDS. To test this hypothesis, we added a few gluconamide crystals to the 10% SDS containing gel which had survived for more than a month. The crystals were not dissolved, and within 3 h many more crystals were formed and the gel rapidly liquefied. The combined temperature-detergent effect therefore relies on the fact that nuclei cannot grow under these conditions; they are thermodynamically unstable.

Solid-state ^2H NMR spectra of the SDS containing gels at 60 °C showed 39% of the gluconamide to be in the isotropic phase as compared to 13% in the pure gels. The concentration of gluconamide was 30%, so that the critical gelation concentration of about 0.8% was always surpassed.

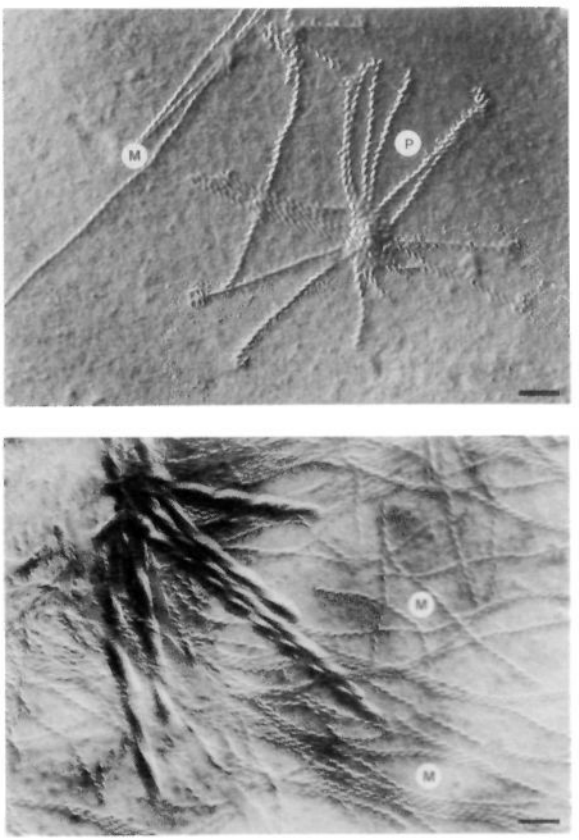

Figure 8. Octadecylmannonamide (**4c**) dissolves in boiling micellar solutions of SDS or dodecylmaltoside (molar ratio 1:2). (a) P- and M-helices are formed within minutes from the SDS solutions at 70 °C. At room temperature they rearrange to bilayer scrolls (not shown).[3] (b) The dodecylmaltoside micellar solutions produce uniform M-helical fibers at room temperature (Pt/C-shadowed, bar = 150 nm).

At higher concentrations of SDS, e.g., a 1:1 molar ratio, no gel was formed. On cooling direct crystallization of gluconamide was observed. The concentration of free micelles for fiber and gel formation was obviously not reached.

Boiling 4% SDS solutions also dissolve *N*-octadecyl-L-mannonamide, which is completely insoluble in water. On cooling long-lived gels were formed. During the gelation process samples for electron microscopy were taken. Surprisingly, at the first appearance of turbidity (70 °C) P- and M-helices were detected (Figure 8a). Such helices have never been obtained from mannonamides, e.g., the octyl homologue **2a**. Probably **4c** is highly hydrated in mixed micelles with dodecylsulfate, and statistical screw dislocations are induced in both directions. M- and P-helices are observed, because the growth process from dodecylsulfate micelles is fast (Figure 8a). During the following gelation process the helices grow to multilayered scrolls (not shown) to lower the surface energy similar as described by Kunitake et al.[7,21] If the aforementioned experiment is repeated with a solution of 0.5% neutral dodecylmaltoside micelles as a solvent, the separation process slows down considerably, and the gelation is retarded. The screw sense of the fibers now becomes uniformly minus (Figure 8b).

Summary and Outlook

The longevity of the gluconamide gels and fibers at temperatures close to the fiber's melting points and in the presence of detergents

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depend on the thermodynamical instability of crystallization nuclei under these conditions. Precipitation can therefore at any time be triggered by the additon of a gluconamide crystal. To our knowledge there is no other heterogeneous system, which has comparable high surface energies, is stable for months, possibly years, and can be destroyed within hours by addition of a crystal. This unique behavior is a clear-cut demonstration of the "chiral bilayer effect" namely the slowness of the formation of enantiomer polar crystal sheets from tail-to-tail micellar bilayers.

Although the gluconamide fibers are well-organized and separate spontaneously, if their stereochemistry is established correctly, they cannot be used directly as skeletons for organized reaction systems. The rigidity of their hydrophobic cores forbids their general use as solvent for redox-active dyes. The flexibility of the chiral head groups, on the other hand, should allow chiral recognition processes by the fiber surfaces. Extended polymerization reactions of the fibers should be most successful, if the cross-linking agent fits into the voids between the head groups and thereby diminishes rotational movements.

Application of gluconamide fibers for the construction of molecular machines therefore relies on the construction of redox-active dyes, which allow an undisturbed fit into the hydrogen-bonded skeleton. Linear polyene amphiphiles containing *N*-alkylamides have already been introduced into these fibers.[21] Work with phenylenediamine and quinone containing hydrophobic chains is in progress.

Experimental Section

Syntheses of *N*-*n*-octyl- and *N*-*n*-octadecylaldonamides. Aldonic acid lactones were either purchased (Sigma) or prepared as described elswhere.[2,3] The *n*-octylamine-*1*,*1*-d_2 was labeled by reduction of *n*-heptylnitrile with lithium aluminum deuteride. Aminolysis of the lactones was performed by heating with equimolar amounts of octylamine or octadecylamine in methanol. All products were crystallized or precipitated from methanol and gave satisfactory spectra (IR, NMR, mass spectra) and elemental analysis.

CMC Measurements. Various amounts of the glyconamides **1a**–**3a** (2–25 mg) were dissolved in 2 mL of hot water (80 °C at glucon and gulonamide, 95 °C at mannonamide). After addition of 10 mL of 2 mM DPH in THF the tubes were incubated for 10 min in the dark to reverse any photoisomerization of DPH and to equilibrate the dye between aqueous solution and micellar core. The measurements were carried out with a Perkin-Elmer MPF-44B fluorescence spectrometer. The excitation wavelength was 358 nm (slit bandwidth 1 nm) and the emission wavelength was 430 nm (slit bandwidth 20 nm). In all experiments 1-cm pathlength quarts cuvettes were used. Some measurements were done with duplicate sets of samples, and average fluorescence was noted.

Differential Scanning Calorimetry (DSC). Glucon-, mannon-, and gulonamide (2.1 mg, 6.8 mmol) in 70 μL of H_2O were measured at temperatures between 0 °C and 110 °C (heating rate 2.5 deg min^{-1}) with a Perkin-Elmer DSC-2C calorimeter. The transition points of gluconamide (73 °C/heating curve, 66 °C/cooling curve) and mannonamide (99 °C/93 °C) were reproducible as well as the melting signal of gulonamide (55 °C). Only the solidification peak of the latter occurred at different temperatures (28 °C, 13 °C, 3 °C).

Sample Preparation for NMR Spectroscopy. For ^2H NMR measurements 60 mg (0.19 mmol) of gluconamide **1b**, 60 mg (0.19 mmol) of gulonamide **3b**, or 6 mg (0.019 mmol) of mannonamide **2b** was dissolved in 0.2 mL of deuterium-depleted water (Sigma, natural abundance $\times 10^2$) containing 2% (respectively 0.2% at mannonamide) of phosphotungstate. The pH was adjusted to 7 with sodium hydroxide. The emulsion was refluxed to yield clear micellar solutions. Gelation occurred on cooling to room temperature. The samples of **1b** were measured in a temperature range from 0–70 °C, the samples of **3b** from −18 °C to 50 °C. Temperature variations were carried out in steps of 10 °C, just below the melting point in steps of 2 °C and 5 °C, respectively. From mannonamide **2b** only one spectrum at 30 °C was recorded, because of its low solubility. At each new temperature the samples were allowed to equilibrate for 15–20 min. The observed spectra and intensity ratios of the powder pattern and the singlet were reversible, independent of temperature variation by heating or cooling.

For ^1H NMR measurements 30 mg (0.1 mmol) of the amides **1a** and **3a** and 10 mg (0.03 mmol) of amide **2a** were prepared as described above by using 0.5 mL of 2% (respectively 0.7% at mannonamide) phosphotungstate in D_2O.

^2H NMR spectra were recorded with a Bruker CXP 300 pulse NMR spectrometer at a frequency of 46.07 MHz. A solid echo pulse technique was employed with pulse durations around 3.3 μs and pulse delay times of about 50 μs. Depending on the signal-to-noise ratio between 1000 and 50 000 transients were accumulated. For ^1H NMR spectra a Bruker WH-250 spectrometer was used.

^{13}C CP/MAS spectra were measured on the same instrument equipped with the adequate attachments.

Gel Preparation for Longevity Measurements. Gluconamide **1a** (20 mg, 65.1 mmol) was dissolved in 1 mL of distilled water (2% w/v) by heating in a water bath at 80 °C. The samples were allowed to cool to either room temperature or to 60 °C, where gelation occurred. Sodium dodecylsulfate (8 mg, molar ratio 2.5:1 and 2 mg, molar ratio 10:1) was added before the samples were heated.

Sample Preparation for Electron Microscopy. Carbon-coated copper grids were dipped into the aged gels of gluconamide **1a** at room temperature and 60 °C, respectively. Negative staining was carried out with 2% (w/v) phosphotungstate at pH = 7. A suspension of 10 mg (0.022 mmol) of mannonamide **4c** was heated in 3.3 mL of bidistilled water containing (a) 4% of the anionic sodium dodecylsulfate and (b) 0.5% of the neutral *n*-dodecyl-β-D-maltoside. During the gelation process, on cooling of the clear micellar solution, sample preparation was carried out by dipping in formvar-coated copper grids (Balzers). The air-dried grids were shadowed by evaporation of platinum/carbon under an angle of 35° by using the Edwards Coating System E 306 A. Electron microscopy was carried out with a Phillips EM 300.