characteristics are also of great importance, for example surface area, adsorption rate of pollutants and oxygen, concentration of surface hydroxyl groups, recombination rate of electron–hole pairs, crystallinity, and so forth. The complex nature of the origin of good photocatalytic properties in combination with our lack of knowledge related to the effects of oxide doping underlines the difficulty to predict the composition of the most active catalyst. The success of this simple study suggests that there may be many more photocatalytically active materials. It also indicates how little we know about the structure–activity relationship for visible-light photocatalysts.

Received: February 22, 2001 [Z16667]

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Rational Design of Low Molecular Mass Organogelators: Toward a Library of Functional *N*-Acyl-1,ω-Amino Acid Derivatives**

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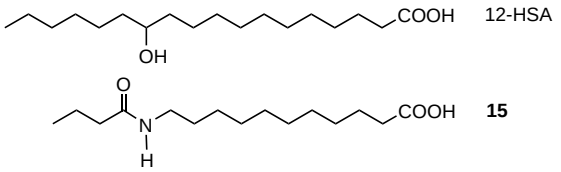
The gelation of organic fluids by low molecular mass organic gelators is a fascinating phenomenon in that it represents a spectacular macroscopic expression of molecular self-assembly.[1, 2] Organogels have especially attracted much interest as a unique class of nanostructured organic materials with far-reaching applications.[1–3] A major challenge that arises thus concerns the elaboration of novel design strategies enabling the synthesis of new series of gelator molecules. In that connection, structurally simple compounds,[4] easy to synthesize and available in large amount from cheap starting materials, are desirable from both fundamental and practical standpoints. Several design approaches have been already proven successful, that are based on the use of various self-recognition units.[5] Hydrogel formation with amphiphilic molecules was also reported recently.[6, 7]

Fatty acid compounds are known to form gelatinous and curd-fiber phases in organic solvents, but typically at high concentrations.[8] Within this series of amphiphile compounds, the behavior of 12-hydroxystearic acid (12-HSA, Scheme 1) attracted special attention.[9] Indeed, this compound displays a remarkably improved gelation ability in organic solvents as compared to analogous molecules lacking a hydrogen bonding group in the hydrophobic chains.[10] It occurred to us that *N*-acyl-1,ω-amino acid compounds presenting similar structural features to 12-HSA could also provide gelation ability,



Scheme 1. Structure of 12-HSA in comparison with the new gelator **15**.

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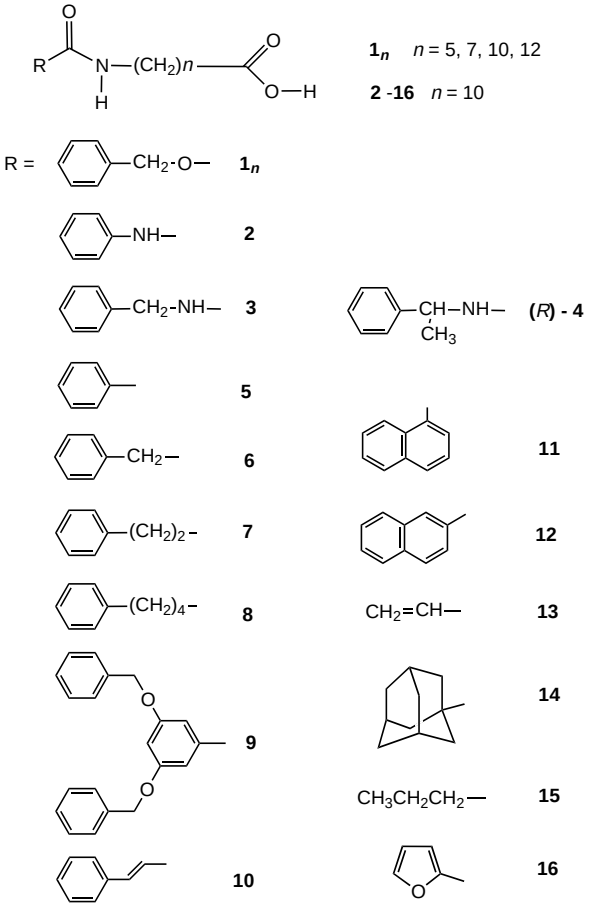
[**] We thank the CNRS, the University Bordeaux 1, La Région Aquitaine, and the Deutsche Forschungsgemeinschaft (DFG, Vo 145/49-1). This work was supported by COST Chemistry in the framework of COST D11 Action (network D11/0015/99).We are also grateful to Dr. Christoph Schalley for mass-spectroscopic characterizations.

  1433-7851/01/4017-3164 $ 17.50+.50/0

particularly those derivatives containing a long aliphatic chain as spacer between the terminal carboxylic functionality and an amide, urethane, or urea group serving as strong, directional hydrogen bonding unit. Our question was if unbranched achiral molecules like *N*-butyroyl-11-aminoundecanoic acid would act as gelators. It should be mentioned that a few studies by different research groups illustrated the formation of fibrous molecular assemblies and gels in the particular case of *N*-acyl derivatives of short amino acids, such as α- or β-alanine, and glutamic acid.[11]

We report herein on the pronounced gelation ability in different organic solvents of a representative series of selected *N*-acyl-1,ω-amino acid compounds, $\mathbf{1}_n$ and **2**–**16**, in which the nature of the pendant *N*-acyl group, the amino acid chain length, and the ionization state of the carboxylic acid functionality differ (Scheme 2). The *N*-benzyloxycarbonyl amino acids, $\mathbf{1}_n$, were investigated as prototypes of urethane derivatives with different chain lengths ($n = 5, 7, 10, 12$). The ureas and amide derivatives **2**–**16** were obtained from amino 11-undecanoic acid ($n = 10$).



Scheme 2. Structures of the compounds $\mathbf{1}_n$ and **2**–**16** investigated in this study.

The neutral carboxylic acid derivatives were found to be insoluble in hot CCl_4 and very soluble in DMF at room temperature (> 20 mg mL^{-1}). Only compounds **13** and **15** were observed to gelate toluene at a concentration of 2×10^{-2} M.

The gelation ability of the sodium salts was investigated with DMF as a solvent, and the results are collected in Table 1.

Table 1. Gelation properties of the sodium salts of *N*-acyl amino acids $\mathbf{1}_n$, **2**–**16** in DMF.[a]

Compound	c [mg mL^{-1}]	Compound	c [mg mL^{-1}]
$\mathbf{1_{10}}$-Na	< 1	**9**-Na	< 6
2-Na	p	**10**-Na	< 1
3-Na	p	**11**-Na	< 1.5
4-Na[b]	< 1.3	**12**-Na	< 0.6
5-Na	< 1	**13**-Na	< 0.4
6-Na	p	**14**-Na	< 1
7-Na	p	**15**-Na	< 6
8-Na	< 3	**16**-Na	< 2

[a] c = minimum gelation concentration (20 °C); p = precipitate.

Efficient gelators of DMF are found in the three classes of compounds. Other aprotic polar solvents, such as DMSO, propylene carbonate, or *N*,*N*-dimethylacrylamide, were also found to be gelled similarly. The minimum gelation concentration in DMF was in the millimolar range; the acrylamide derivative **13**-Na is the most efficient as only 0.04 wt % is sufficient to immobilize DMF at room temperature. Gelation was observed to be fully thermoreversible, the gel–sol transition for a DMF gel with compound **12**-Na, for example, being observed at about 72 °C at 4×10^{-3} M. Typically, a DMF gel of $\mathbf{1_{10}}$-Na was observed to remain stable and transparent for more than one year in a stoppered tube. The data in Table 1 also show that the nature of the covalent link between the amide carbonyl functionality and the aromatic endgroup is critical for the observed gelation. Indeed, amide compounds **6**-Na and **7**-Na with one and two methylene groups, respectively, do not form a gel whereas **5**-Na and **8**-Na, incorporating zero and four methylene units respectively, do gelate DMF. In this regard, it is remarkable that gelation is observed for the chiral urea (*R*)-**4**-Na but not for the achiral analogue **3**-Na, which lacks the methyl substituent. Urethane compounds with a short chain ($n = 5$, 7) gelate DMF but at a higher concentration (about 10 mM, 4 mg mL^{-1}) as compared to the longer analogues ($n = 10$, 12). Noticeably, the gelation propensity is also retained for those compounds that bear a bulky substituent, such as dendron and adamantane moieties in **9**-Na and **14**-Na, respectively. The sodium salts were observed to be insoluble in apolar solvents (cyclohexane, toluene, CCl_4). However, when one drop of methanol was deposited onto the solid gelator compound in a test tube, subsequent addition of these solvents caused instant gelation at room temperature (methanol content 5–7 vol %). The compounds described here are shown to gelate preferably as their sodium carboxylate form. It is likely that both sodium cation coordination and hydrogen bond formation play a major role in the establishment of directional aggregates, as sketched in Scheme 3 on the basis of crystallographic data obtained for long-chain carboxylates.[6]

This study shows the versatile construction of new gelator systems based on the *N*-acyl amino acid scaffold by incorporating appropriate molecular segments including chiral ones. A combinatorial approach could be helpful to generate a great diversity of *N*-acyl amino acid gelators that can be obtained simply in one step from commercially available amino acids and activated acids libraries. They are thus easy to

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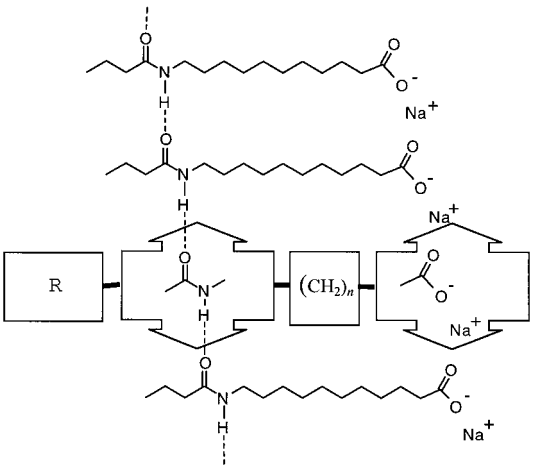

Scheme 3. Illustration of one-dimensional self-aggregation in the case of sodium *N*-acyl aminocarboxylate compound **15**. R represents a pendant aliphatic chain or aromatic group.

prepare in large amounts and at low cost. These features open exciting perspectives toward the development of functional material based on this family of organogelators.

Experimental Section

The synthesis of compounds $\mathbf{1}_n$ and **2**–**16** was performed according to classical procedures and will be published elsewhere. Chemicals and solvents were used as received.

Received: February 23, 2001 [Z16672]

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A New Method toward Microengineered Surfaces Based on Reactive Coating**

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The control of engineered microenvironments on device surfaces has been addressed by several approaches including soft lithographic methods, such as microcontact printing (μCP) and micromolding (MIMIC).[1] These procedures have been used for the formation of a wide range of surface patterns, for example protein and cell arrays,[2] and for micro- and nanofabrication of devices. Potential applications include the regulation of cell shapes,[3] the development of microelectronic elements, such as optical displays,[4] circuits, or lasers,[5] and the fabrication of complex three-dimensional microstructures[6] or microfluidic devices.[7] A key step is generally the spatially controlled self-assembly of monolayers on a substrate.[8] Although several systems have been investigated, only assemblies of siloxanes on silicon oxide[9] and of alkanethiolates on gold[10] are widely exploited. Biomedical devices are however mostly manufactured from polymers and metals other than gold. For these materials, the microengineering of patterns is very challenging and only addressed in a few cases.[11] The main limitation is the lack of sufficient and homogeneously distributed functional groups on the substrate surface being necessary for the build-up of further structural elements. Treatment with high-energy sources, such as plasma,[12] laser,[13] or ion beams,[14] has been used to create functionalized surfaces for biomedical systems. Recently, poly(ethylene terephthalate) was surface modified via a multistep synthesis to generate a surface for the μCP of biological ligands.[15] Alternatively, CVD-based polymer coatings were used in order to provide amino- or hydroxyl-functionalized surfaces for the conjugation of biomolecules.[16] Although CVD polymerization has been known for more than 30 years,[17] the exploitation of functionalized [2.2]paracyclophanes for CVD polymerization was realized only recently.[18]

Amino- or hydroxyl-functionalized poly(*para*-xylylene) coatings require an additional activation step for linkage of proteins or ligands. Typically, bivalent spacers, such as hexamethylene diisocyanate, are used for amino- or hydroxyl-functionalized polymers.[16] The additional activation step not only limits the feasibility of microengineering but also causes the contamination of the substrate with organic solvents and volatile chemicals. These contaminations reduce crucial advantages of CVD coatings, such as their low intrinsic cytotoxicity due to the absence of harmful solvents, initiators, or accelerators during polymerization. Therefore, an one-step

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[**] This work was supported by the Fonds der Chemischen Industrie, the National Science Foundation, and the National Institutes of Health.

  1433-7851/01/4017-3166 $ 17.50+.50/0