Influence of an Odd-Even Relationship on the Aggregation Modes of "Gemini"-type Cholestrol-Based Gelators and Their Transcription into Silica Gel

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Four "gemini"-type cholesterol-based gelators 1_n were synthesized. They acted as versatile gelators of organic fluids. The xerogels show lamellar structures for 1_2 and 1_4 and fiber structures for 1_3 and 1_5 according to the even or odd number of alkyl chains between two nitrogens. The difference in these organogel supramolecular structures has successfully been transcribed into the silica structures by sol-gel polymerization of tetraethoxysilane (TEOS). These results indicate that the novel silica structures can be created by transcription of various superstructures in organogels as a template through the hydrogen-bonding interaction.

The use of organic molecules, assemblies, and supramolecular systems in the development of novel inorganic materials continues to offer new and exciting alternatives to conventional synthetic strategies.[1] As possible templates, protein, multicellular superstructures, surfactants, and DNA have been utilized to create novel structures of inorganic materials.[2] Recently, increasing attention has been paid to low molecular-weight compounds that can efficiently gelate various organic solvents.[3-15] These phenomena are interesting in that aggregates formed by non-covalent interactions are responsible for the gelation, and therefore, can provide a variety of superstructures reflecting each gelator structure. The certain cholesterol gelators can be classified into two different aggregation modes, which have fibrous or lamellar structures. To the best of our knowledge, however, there has been no general guideline to produce fibrous or lamellar aggregates in organogels. In this communication, we report for the first time that these two different aggregation modes can be produced by an odd-even effect in "gemini"-type cholesterol-based gelators, which can be successfully transcribed into the silica by sol-gel polymerization of gelated tetraethoxysilane (TEOS).

We already found that cationic charge density along the template aggregates is an important factor of the template effects to transcribe the organogel structure into silica. In addition, Pinnavaia and co-workers[16] recently reported that the novel structure of mesoporous silica is produced by the hydrogen-bonding interaction between diamine surfactant as organic template and TEOS as inorganic material in the solution phase. It suggests that unique morphology of inorganic materials can be controlled using the hydrogen-bonding interaction between organic template and inorganic materials. Thus, our initial motivation to prepare cholesterol-based gelators (1_n) was not only to observe influence of an odd-even effect on the aggregation modes but also to prepare the tubular structure of the silica through the cationic-charge effect and/or the hydrogen-bonding interaction effect operating between organic gelators and TEOS oligomers.

Compounds 1_n were synthesized according to the similar

$$1_n = \begin{pmatrix} 1_2 : n=2, & 1_3 : n=3 \\ 1_4 : n=4, & 1_5 : n=5 \end{pmatrix}$$
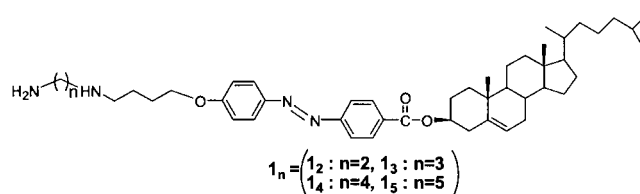
method described previously[15] and identified by IR, ^{1}H NMR, ^{13}C NMR, MS(SIMS) spectral evidence and elemental analyses.

Gelation ability of 1_n was examined in 12 organic solvents. These gelators could gelate several solvents such as 1-butanol, 1-hexanol, 1-octanol, DMF, DMSO, and aniline. To obtain visual insights into aggregation mode, the superstructures constructed in organogels were observed by SEM. Very surprisingly, the gels formed by the four gelators were classified into two different structures. Compounds 1_2 and 1_4 which have the even number of methylene units between NH and NH_2, resulted in a translucent organogel with aniline. The SEM image did not show the fibrous structure characteristic of organogel systems but rather featured the film-like aggregates with 60–330 nm thickness and a few μm length, which probably consist of the lamellar structure (Figures 1a and 1c). It is noteworthy that

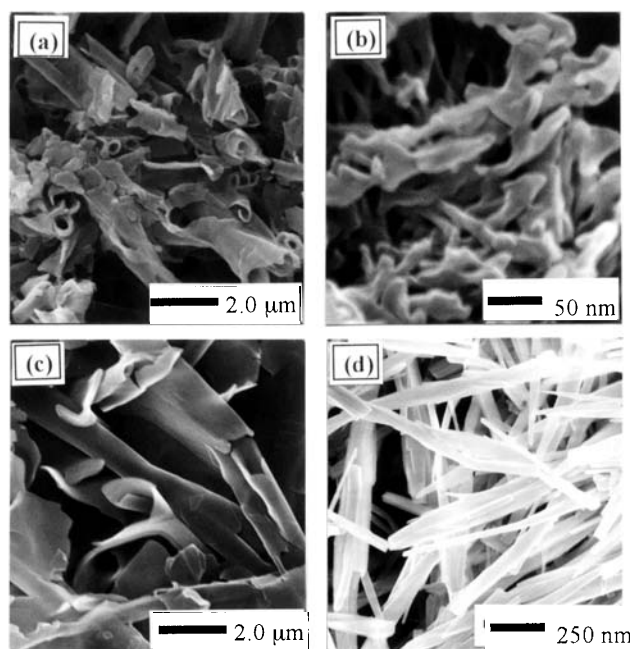**Figure 1**. SEM pictures of xerogels (a) 1_2, (b) 1_3, (c) 1_4, and (d) 1_5 obtained from aniline.

some films are curved to form a pseudo-cylindrical structure. In contrast, 1_3 and 1_5, which have the odd number of methylene units between NH and NH_2, featured the fibrous structures with 20–50 nm and 10–70 nm diameter for 1_3 and 1_5, respectively (Figures 1b and 1d). These novel findings indicate that the organogel structure can be predicted according to the number of methylene units between NH and NH_2. The clear difference between the odd-numbered gelators and the even-numbered gelators implies that the aggregation mode is crucially governed by the molecular packing of the terminal groups.

We carried out sol-gel polymerization of 1_n in 1-butanol according to the method described previously.[14,15] For example, 1_2 (5.8×10^{-6} mol) was dissolved in a medium for sol-gel polymerization: 1-butanol (98 mg) / TEOS (16 mg) / water (5.7 mg) / benzylamine (5.6 mg). The sample was sealed in a glass tube and left at ambient temperature for 7 days. Subsequently, the sample was heated at 200 °C for 2 h, 500 °C for 2 h under a nitrogen atmosphere and then kept at 500 °C under the aerobic conditions for 4 h. We observed the SEM pictures of the silica obtained from 1_n before calcination (the pictures are not shown here).[17] The silica obtained from 1_2 and 1_4 possesses the roll-paper-like hollow structure arising from the template organogel films, which has 380–400 nm inner diameter and 40–60 nm wall thickness. On the other hand, the resultant silica obtained from 1_3 and 1_5 featured the fibrous structure. The results suggest that the oligomeric silica species are adsorbed onto these wide aggregates mainly by the hydrogen-bonding interaction between TEOS and amine groups of the gelators.[16] After calcination by which organic compounds are removed by combustion, the morphology of the silica obtained from 1_2 and 1_4 was observed in a similar fashion to those before calcination (Figures 2a and 2c), whereas the resultant silica obtained from 1_3 and 1_5 showed the fibrous structure which has 15–40 nm and

50–150 nm of inner and outer diameter, respectively (Figure 2b and 2d).[18] One may expect a slight shrinkage of the silica during the calcination process. These results clearly indicate that the organogel structure is finely transcribed into the silica mainly due to the hydrogen-bonding interaction, and oligomeric silica species are adsorbed onto the gelator surface.

In conclusion, the present paper has demonstrated for the first time that the structure of organic gelators can be classified into the lamellar or the fiber structure by the number of methylene units between NH and NH_2. The novel silica structures are created by the hydrogen-bonding interaction between the lamerllar or the fibrous structure of gelators. We believe that various novel silica structures can be further prepared by transcription using various superstructures in organogels as a template.

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17   The silica show lamerllar structures from 1_4 and fiber structures from 1_5 in aniline, respectively.
18   The inner and outer diameter were observed by TEM (for examples, TEM pictures of the silica obtained from 1_2 and 1_5 show in graphical abstract).
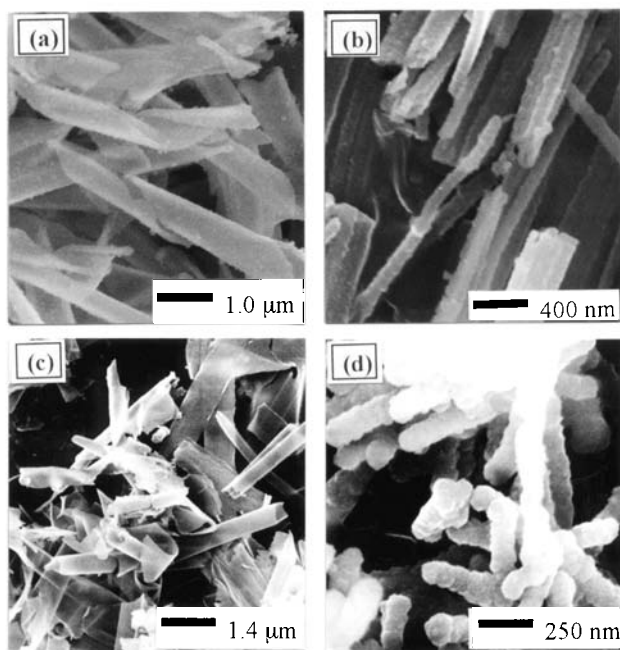
Figure 2. SEM pictures of the silica obtained from (a) 1_2, (b) 1_3, (c) 1_4, and (d) 1_5 in 1-butanol.