Template Effect of Cholesterol-based Organogels on Sol-Gel Polymerization Creates Novel Silica with a Helical Structure

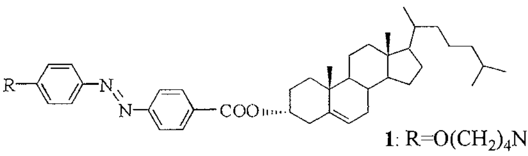
Yoshiyuki Ono, Kazuaki Nakashima, Masahito Sano, Junichi Hojo,† and Seiji Shinkai*
Chemotransfiguration Project, Japan Science and Technology Corporation (JST), 2432 Aikawa, Kurume, Fukuoka 839-0861
†Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581

(Received July 15, 1999; CL-990625)

The helical structure was introduced into the silica for the first time utilizing a template effect of a cholesterol-based organogel system. It was shown that the cationic charge dilutely distributed in the organogel fibers plays an essential role.

A diversity of supramolecular structures can be created, not only in Nature but also in an artificial system, by self-assembly of designed organic building blocks. In general, creation of such diverse supramolecular structures seems to be very difficult or nearly impossible in inorganic materials. Is there any innovative method by which inorganic materials can be self-assembled into the ordered supramolecular structures? The sole method which can satisfy this requirement would be a template effect of organic surfactant molecules.[1]

Recently, increasing attention has been paid to low molecular-mass compounds that can gelate various organic solvents efficiently.[2-12] These phenomena are interesting in that the fibrous aggregates formed by non-covalent interactions are responsible for the gelation. In particular, cholesterol-based gelators, which can form stable gels using only non-hydrogen-bonding interactions, show an excellent gelation ability towards a wide variety of organic solvents at sufficiently low concentrations.[6-10,12] In addition, the resulting gels have chirally oriented structures which are imparted from the characteristic cholesterol skeleton. Through this study we found that even liquid silanol derivatives can be gelated by some cholesterol-based gelators.[8] It thus occurred to us that if the sol-gel polymerization of the silanol derivatives proceeds in the organogel state, the gelator fibrils should act as a template which eventually creates a void in the resultant silica. After trial-and-error, we found that only when the gelator carries the cationic charge (as in **1**), the gelator fibrils can survive in the sol-gel process and construct a tubular structure in the fibrous silica.[13, 14] We carefully investigated the influence of the cationic charge density on the transcribed silica structure. Very surprisingly, we have found that "chiral hollow fiber silica with a helical structure" is produced only under the limited sol-gel polymerization conditions. To the best of our knowledge, this is the first example for the creation of "chirality" in the silica structure.[15]



1: R=$O(CH_2)_4NMe_3^+Br^-$
2: R=$O(CH_2)_3Me$

Sol-gel polymerization was carried out as follows: **1** and **2** (in prescribed mol%; total 2.48×10^{-6} mol) were dissolved in CH_2Cl_2 (90.5 mm^3). To these solutions were added $MeCO_2H$ (122.5 mm^3), water (6.2 mm^3) and TEOS (20.3 mm^3) in this order. The resultant solutions were evaporated *in vacuo* until CH_2Cl_2 was removed (monitored by the mass decrease). Since the mixture of $MeCO_2H$-water-TEOS was gelated under these conditions, the solutions changed to gels after removal of CH_2Cl_2 which acted as a good solvent for the gelators. After a sol-gel reaction of TEOS for 10 days, they were heated at 200 ℃ for 1 h under an N_2 stream and then at 500 ℃ for 2 h. Finally, they were heated at 500 ℃ for 4 h in air for the pyrolytic decomposition of the gelators.

As shown by a SEM image in Figure 1A, sol-gel polymerization of TEOS in the solution gelated by **1** resulted in well-grown fibrous silica and the tube edges contained cavities. As shown by a TEM image in Figure 2A, these fibers have a tubular structure with inner diameters of 10 – 200 nm and outer diameters of 50 – 300 nm. It is known that the organic gelator fibrils of **1** act as a template in the sol-gel process.[13] When neutral **2** was mixed with cationic **1**, the hollow fiber silica still resulted at R [= **1**/(**1**+**2**)] = 25-100% although the size became somewhat smaller (outer diameter of *ca.* 200 nm: Figure 1B). At R = 1-10%, on the other hand, the fibrous silica resulted in a novel helical structure (Figure 1C). As shown in a TEM image in Figure 2B, this helical silica also has a tubular structure with inner diameters of 10-15 nm. At R<1%, the fibrous silica was no longer yielded and the resultant silica showed the conventional

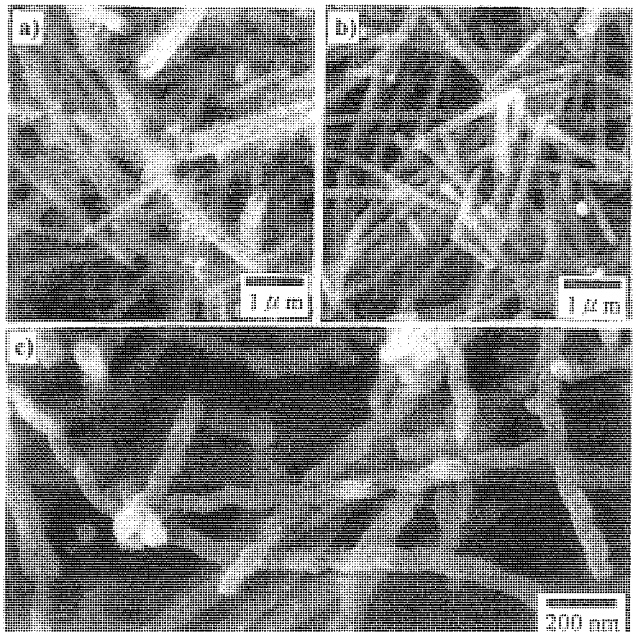


Figure 1. SEM images of silica structures prepared using the mixture of **1** and **2** as a template. Mol ratios of **1** are 100% (a), 25% (b), and 10% (c).

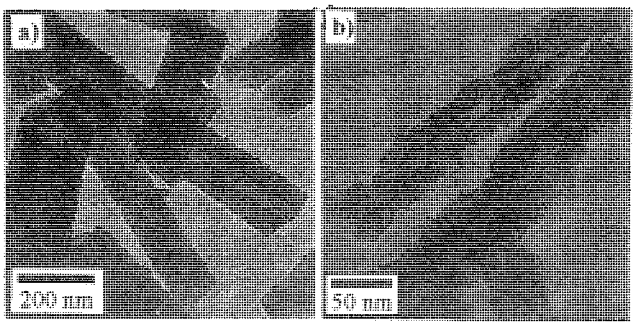


Figure 2. TEM images of hollow fiber silica prepared using **1** as a template, a), and helical hollow fiber silica using the mixture of **1** (10 mol%) and **2**, b).

granular silica structure. The results indicate that the novel helical silica is obtained only under the very limited conditions of R = 1-10%.

Careful examination of these SEM and TEM pictures reveals that (i) the observed helical silica fibers are all right-handed, (ii) the helical pitch is 100-200 nm, and (iii) the inner diameter (*ca.* 10 nm) shows a relatively narrow distribution. In particular, the finding (i) supports the view that the helical structure results from the template effect of the "chiral" cholesterol-based gelators but not from the crystallization or shrinkage in the silica formation process. Such a non-templated process should yield right-handed and left-handed fibers in a 1:1 ratio, even if they are formed.

To look for such a organogel template used for the transcription we took a number of SEM and TEM pictures but eventually could not find any organogel fiber with a helical structure. Figure 3 shows a TEM image of an organogel which was stained before the organogel fiber growth. One can recognize many stripes in a gigantic organogel fiber. When it was stained after the organogel fiber growth, these stripes could not be observed. The size of these stripes is comparable with that of the helical silica fibers. We now consider, therefore, that the incipient fibers which appear at the early stage of organogel fiber growth were stained to form the stripe structure in Figure 3. Likewise, these incipient fibers could be transcribed by sol-gel polymerization of TEOS. Conceivably, these fibers possess some motif to create the helical structure. When the **1** content is high, the high cationic charge density along the gel fibers would induce a random adsorption of silica. On the other hand, at R = 1-10% the cationic charge in **1** is diluted with **2** into an oriented structure and would act as a reaction site for silica polymerization.

To obtain a further insight into the silica propagation process we took TEM pictures as a function of polymerization time (Figure 4). In order to slow down the polymerization velocity the TEOS concentration was reduced to 10% of the standard concentration. At an early stage, silica particles with the anionic charge are adsorbed onto the organogel fibrils with the cationic charge (Figure 4A). At this stage, however, the helical structure cannot be seen clearly. With the polymerization time the fiber surface gradually becomes rough (Figure 4B). Conceivably, the progress of sol-gel polymerization enforces the tight packing of silica particles and makes the silica fibers stiff. Under such tightly-packed conditions the most stable structure which can relax the steric crowding would be a helical one and the twisting direction would be governed by the chirality in the cholesterol-based gel fibers. Finally, the novel silica with a chiral structure appears (Figure 4C).

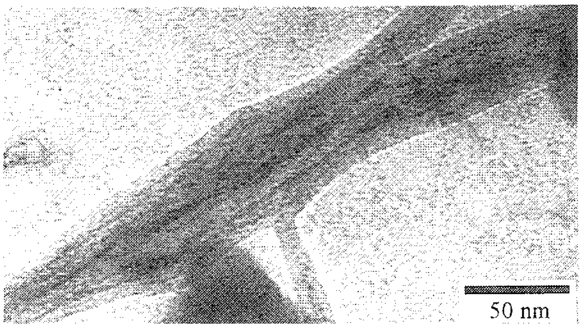


Figure 3. A TEM image of an organogel fiber, mol ratio of **1** is 10%, stained by sodium phosphotungstate.

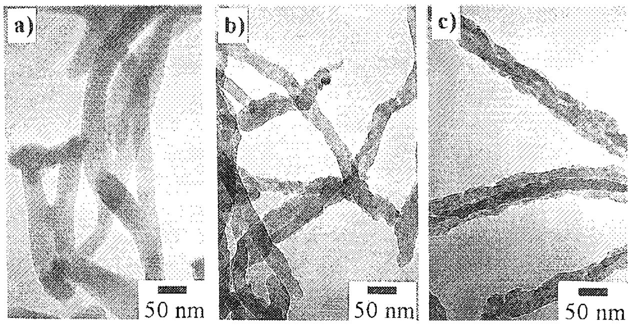


Figure 4. The development of helical hollow fiber silica with a reaction time is shown in TEM images: 1 h (a), 6 h (b), and 3 days (c).

In conclusion, the present study has demonstrated that "chirality" which is characteristic of organic compounds and assemblies can be created also in inorganic compounds. The key-point is to transcribe the chirality in organogel fibers into silica utilizing the electrostatic interaction. We believe that this concept is very essential and applicable to many other transcription systems.

References and notes

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C.Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992); H. Yang, N. Coombs, G. A. Ozin, *Nature* **386**, 692 (1997).
2 E. J. de Vries and R. M. Kellogg, *J. Chem. Soc., Chem. Commun.*, **1993**, 238; M. de Loos, J. van Esch, I. Stokroos, R. M. Kellogg, and B. L. Feringa, *J. Am. Chem. Soc.*, **119**, 12675 (1997).
3 M. Aoki, K. Nakashima, H. Kawabata, S.Tsutsui, and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 347.
4 K. Hanabusa, A. Kawakami, M. Kimura, and H. Shirai, *Chem. Lett.*, **1997**, 191 and references therein.
5 J.-E. S. Sohna and F. Fages, *Chem. Commun.*, **1997**, 327.
6 E. Otsuni, P. Kamaras, and R. G. Weiss, *Angew. Chem., Int. Ed. Engl.*, **35**, 1324 (1996) and references therein.
7 P. Terech, I. Furman, and R. G. Weiss, *J. Phys. Chem.*, **99**, 9558 (1995).
8 K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, and S. Shinkai, *J. Am. Chem. Soc.*, **116**, 6664 (1994).
9 T. D. James, K. Murata, T. Harada, K. Ueda, and S. Shinkai, *Chem. Lett.*, **1994**, 273.
10 S. W. Jeong, K. Murata, and S. Shinkai, *Supramol. Sci.*, **3**, 83 (1996).
11 T. Brotin, R. Utermöhlen, F. Fages, H. Bouas-Laurent, and J. -P. Desvergne, *J. Chem. Soc., Chem. Commun.*, **1991**, 416
12 For recent comprehensive reviews, see P. Terech and R. G. Weiss, *Chem. Rev.*, **97**, 3133 (1997); S. Shinkai and K. Murata, *J. Mater. Chem.* (*Feature Article*), **8**, 485 (1998).
13 Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, J. Hojo, and S. Shinkai, *Chem. Commun.*, **1998**, 1477
14 Y. Ono, Y. Kanekiyo, K. Inoue, J. Hojo, and S. Shinkai, *Chem. Lett.*, **1999**, 23.
15 Although several inorganic materials with a helical structure were reported, they were not examples of the chiral template method as shown in this report. K. Robbie, M. J. Brett and A. Lakhtakia, *J. Vac. Sci. Technol. A*, **13**, 2991 (1995); Y. Akiyama, F. Mizukami, Y. Kiyozumi, K. Maeda, H. Izutsu, and K. Sakaguchi, *Angew. Chem. Int. Ed.*, **38**, 1420 (1999).