# Organic gels are useful as a template for the preparation of hollow fiber silica

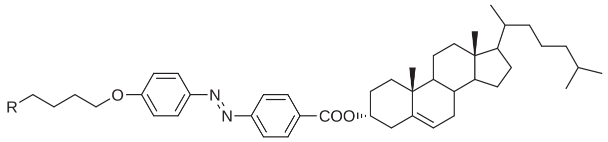
**Yoshiyuki Ono,[a] Kazuaki Nakashima,[a] Masahito Sano,[a] Yasumasa Kanekiyo,[a] Kazuhiko Inoue,[a] Junichi Hojo[b] and Seiji Shinkai*[a]†**

[a] *Chemotransfiguration Project, Japan Science and Technology Corporation (JST), 2432 Aikawa, Kurume, Fukuoka 839-0861, Japan*
[b] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan*

**A novel mesoporous silica with a tubular structure has been prepared using organic gel fibers as a template.**

Increasing attention has been paid to low molecular-mass compounds that can gelatinize various organic solvents efficiently.[1–11] 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.[5–9,11] 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 gelatinized by some cholesterol-based gelators.[7,12] It thus occurred to us that if the sol–gel polymerization of the silanol derivatives proceeds in the organic gel state, the gelator fibrils should act as a template which eventually creates a void in the resultant silica. After trial-and-error, we have found that under certain reaction conditions the gelator fibrils survive in the sol–gel process and construct a tubular structure in the fibrous silica.

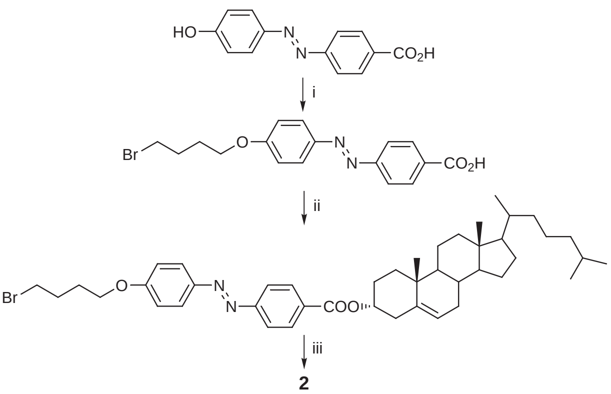
It is known that compound **1** can gelatinize tetraethoxysilane (TEOS).[12] First, this gel was polymerized under acidic or basic reaction conditions. SEM observation showed, however, that the structure which might be constructed using this gelator fibrils as a template was not found in the resultant silica. Hence, we newly synthesized compound **2** which contains a quaternary ammonium cation like conventional cationic surfactants generally used as templates for sol–gel polymerization.[13,14] Compound **2** was synthesized according to Scheme 1 and identified by IR and $^1$H NMR spectral evidence and elemental analysis. Since $PPh_3$ and azodicarboxylic acid diethyl ester were used for the condensation with cholesterol, the C-3 atom has the unnatural inverted (*R*)-configuration.[7]



R = H **1**, R = $NMe_3^+Br^-$ **2**

The gelation ability was tested using several organic solvents (Table 1). It is seen from Table 1 that **2** is not very soluble in organic solvents but can gelatinize some solvents such as MeOH, EtOH and $MeCO_2H$. As a gelator, therefore, **2** is not so versatile as **1**. Fig. 1 shows a SEM image of a dried gel prepared from $MeCO_2H$ (3.0 mass%). Well grown fibrils with diameters of 50–200 nm are observed in this photograph.

Sol–gel polymerization was carried out as follows: **2** (5.0 mg) was dissolved in $CH_2Cl_2$ (0.3 g). To this solution were added $MeCO_2H$ (0.32 g), TEOS (0.045 g) and water (0.016 g) in this order. The resultant solution was evaporated *in vacuo* until the $CH_2Cl_2$ was removed (monitored by the mass decrease) to give a turbid acetic acid gel. This gel was sealed in a glass tube and left at 20 °C for 10 days. We also prepared a reference sample which was treated according to the same procedure in the absence of **2**. After 10 days, both mixtures were totally solidified, indicating that sol–gel polymerization of TEOS proceeded sufficiently. In order to preserve the original organic gel structure and the formed silica structure they must be dried under mild conditions. Thus, the products were dried at room temp. for 2 days to remove $MeCO_2H$ and water. Subsequently,



**Scheme 1** *Reagents and conditions*: i, 1,4-dibromobutane, KOH, EtOH, reflux, 15%; ii, cholesterol, $PPh_3$, azodicarboxylic acid diethyl ester, THF, 20 °C, 18%; iii, $NMe_3$, THF, 20 °C, 69%

**Table 1** Gelation ability of **1** and **2**[a]

| Solvent | **1**[b] | **2** |
|---|---|---|
| *n*-Hexane | G | I |
| Toluene | S | I |
| Dichloromethane | S | S |
| Chloroform | S | S |
| Diethyl ether | G[c] | I |
| Tetrahydrofuran | S | I |
| Acetone | G | I |
| Methyl ethyl ketone | G | I |
| Acetonitrile | SG[d] | I |
| Methanol | SG | G |
| Ethanol | SG | G |
| Acetic acid | SG | G |
| *n*-Propylamine | S | I |
| Diethylamine | Gf[e] | I |
| Benzylamine | — | G[c] |
| TEOS | G | I |
| Water | I | I |

[a] The solution (5 mass%) was warmed and then cooled to 4 °C to grow the gel: G = stable gel formed at room temperature, S = solution, I = insoluble. [b] Cited from refs. 7 and 12. [c] The gel was formed at 4 °C but turned into a solution at room temp. [d] Super-gelator in which the gel was formed at a concentration of < 1 mass%. [e] Gel formed when cooled in a refrigerator (at −6 °C) and was stable at room temp.

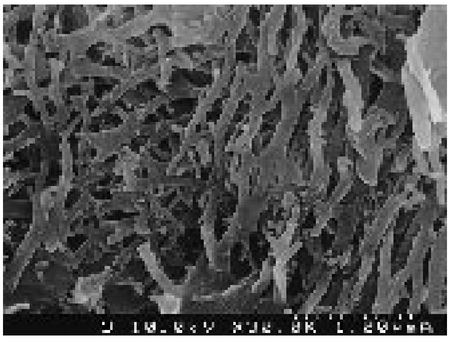


**Fig. 1** SEM image for the gel of **2**–$MeCO_2H$: the gel was frozen in liquid $N_2$ and dried under reduced pressure for 2 h

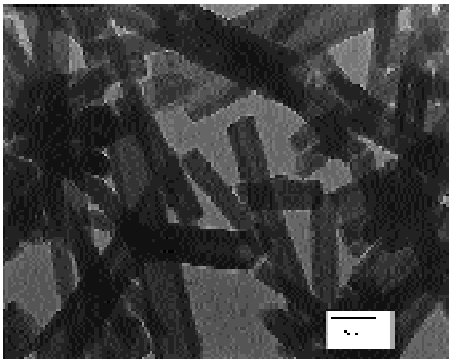


**Fig. 2** TEM image for the silica (sample B) with a tubular structure (125 kV Hitachi H7100 TEM)

they were heated at 60 °C for 5 h *in vacuo* in order to entirely remove residual liquid and to accelerate the TEOS polymerization. At this stage a portion of the samples was subjected to SEM observation (sample A). They were further heated at 200 °C for 6 h under an $N_2$ stream for the polymerization and the removal of the residual stress evolved by shrinkage of the silica network. Finally, they were heated at 500 °C for 2 h under an $N_2$ stream and for 4 h in air (sample B) for the pyrolytic decomposition of **2**.

The SEM image of sample B is shown in the Graphical Abstract. It is clearly seen that sol–gel polymerization results in well grown fibrous silica and very interestingly, the tube edges contain cavities. In order to view the inside of the strand we obtained a TEM image (Fig. 2). It is clearly seen that these fibers have a tubular structure with inner diameters of 10–200 nm. Although the silica may shrink to some extent during calcination, the size is nearly comparable with that of the organic gelator fibrils (50–200 nm: Fig. 1). On the other hand, sample A obtained after treatment at 60 °C also gave fibrous silica but the tubular structure was not observed in the SEM picture. These results indicate that the organic gelator fibrils of **2** act as a template in the sol–gel process, create the tubular structure and finally are removed by pyrolysis at 500 °C.

Here, we consider why **2** can act as the template while **1** cannot although both gelators aggregate into fibers in the organic solvents. When the sol–gel polymerization is carried out in $MeCO_2H$, the propagation species is considered to be anionic.[15,16] Hence, the oligomeric silica species are adsorbed onto the cationic gelator fibrils and the polymerization further proceeds along these fibrils. This propagation mode can eventually yield fibrous silica with tubular structure. This proposal is further supported by the effect of added alcohol: when the sol–gel polymerization was initiated in **2**–$MeCO_2H$–TEOS–$H_2O$–EtOH (1 : 63 : 10 : 4 : 22, m/m), the resultant silica had a well developed fibrous network structure but tubular structure was not observed (SEM). Since EtOH facilitates the polymerization, the resultant silica becomes the network structure but cannot construct the isolated silica fibers.[16]‡ In contrast, the organic gelator fibrils of **1** without the cationic charge cannot adsorb the oligomeric silica species even in the absence of EtOH, so that the resultant silica showed only the granular structure (SEM). Similar granular structure was also observed for the silica obtained in the absence of the gelator.

In conclusion, the present paper has demonstrated a novel application of organic gels as a template to prepare a novel porous silica with tubular structure.

We thank Dr P. C. Ewbank for helpful discussions.

## Notes and References

† E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

‡ It is not yet clear if this network silica also has the tubular structure. The sample is too thick to view the inside with TEM.

1 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.,* 1997, **119**, 12 675.

2 M. Aoki, K. Nakashima, H. Kawabata, S. Tsutsui and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2,* 1993, 347.

3 K. Hanabusa, K. Okui, K. Karaki, T. Koyama and H. Shirai, *J. Chem. Soc., Chem. Commun.,* 1992, 1371; K. Hanabusa, A. Kawakami, M. Kimura and H. Shirai, *Chem. Lett.,* 1997, 191 and references therein.

4 J.-E. S. Sohna and F. Fages, *Chem. Commun.,* 1997, 327.

5 E. Otsuni, P. Kamaras and R. G. Weiss, *Angew. Chem., Int. Ed. Engl.,* 1996, **35**, 1324 and references therein.

6 P. Terech, I. Furman and R. G. Weiss, *J. Phys. Chem.,* 1995, **99**, 9558 and references therein.

7 K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda and S. Shinkai, *J. Am. Chem. Soc.,* 1994, **116**, 6664 and references therein.

8 T. D. James, K. Murata, T. Harada, K. Ueda and S. Shinkai, *Chem. Lett.,* 1994, 273.

9 S. W. Jeong, K. Murata and S. Shinkai, *Supramol. Sci.,* 1996, **3**, 83.

10 T. Brotin, R. Utermöhlen, F. Fages, H. Bouas-Laurent and J.-P. Desvergne, *J. Chem. Soc., Chem. Commun.,* 1991, 416.

11 For recent comprehensive reviews, see: P. Terech and R. G. Weiss, *Chem. Rev.,* 1997, **97**, 3133; S. Shinkai and K. Murata, *J. Mater. Chem.* (*Feature Article*), 1998, **8**, 485.

12 K. Murata, Ph.D. Thesis, Graduate School of Engineering, Kyushu University, 1997.

13 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.

14 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.,* 1992, **114**, 10 834.

15 Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth and G. D. Stucky, *Nature*, 1994, **368**, 317.

16 C. J. Brinker and G. W. Scherer, *Sol–Gel Science,* Academic Press, San Diego, 1990, p. 97.

*Received in Cambridge, UK, 15th April 1998; 8/02829J*