COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Selective formation of siloxane-based hybrid cages with methylene groups in the frameworks†

Atsushi Shimojima*[a] **and Kazuyuki Kuroda***[a,b]

[a] *Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo, 169-8555, Japan. E-mail: a-shimo@kurenai.waseda.jp; kuroda@waseda.jp; Fax: +81-3-5286-3199; Tel: +81-3-5286-3199*
[b] *CREST, Japan Science and Technology Agency (JST), Japan*

Received (in Cambridge, UK) 3rd August 2004, Accepted 24th August 2004
First published as an Advance Article on the web 14th October 2004

A new class of cage-like oligomers were selectively formed by hydrolysis and polycondensation of a methylene-bridged bistrialkoxysilane precursor in the presence of tetramethylammonium hydroxide, which led to the creation of novel silica-based hybrid materials.

Hybrid inorganic–organic materials with well-defined architectures have received increasing scientific and technological interests. Hydrolysis and polycondensation of organoalkoxysilanes $R[\text{–}Si(OR')_3]_n$ is a convenient way to prepare silica-based hybrid materials, however, the difficulty in regulating the polycondensation often results in the formation of amorphous solids. Great efforts have therefore been made to control the structures of the hybrids at various length scales,[1,2] which is very important as a bottom-up approach of nanomaterials design.

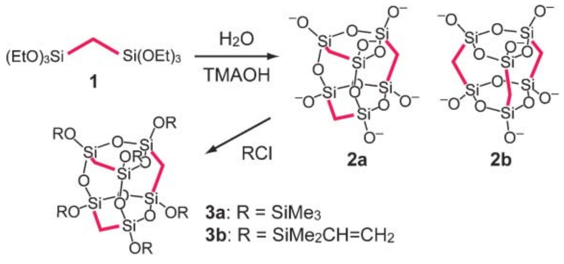
The oligomers with cage-like frameworks are of particular significance because of their well-defined geometries that are useful for scaffolds or building blocks to create new materials.[3–5] Several types of siloxane cages with various organic groups attached to the cage corners have been prepared by the controlled hydrolysis and polycondensation of trifunctional organosilanes.[6] However, their yields are usually low, and possible framework structures are still limited. On the other hand, it is well-known that silicate anions with cage structures such as double-three- and double-four-membered siloxane rings (D3R and D4R) are predominantly formed in aqueous solutions containing quaternary ammonium hydroxides.[7] This is a highly efficient route to cage-like silicates, inspiring us to explore whether organosilane precursors can form cage-like species in a similar way. Until now, such a route has not been realized, though partial replacement of SiO_4 units in D4R cages by CH_3SiO_3 units was reported.[8]

Here we report the selective formation of novel cage-like hybrids (**2a** and **2b**) by hydrolysis and polycondensation of bis(triethoxysilyl)methane [$(EtO)_3Si\text{–}CH_2\text{–}Si(OEt)_3$] (**1**) in the presence of tetramethylammonium hydroxide (TMAOH) (Scheme 1). Bistrialkoxysilane precursors, $(R'O)_3Si\text{–}R\text{–}Si(OR')_3$, have been used to prepare hybrid materials whose frameworks consist of both Si–O and Si–C bonds,[9] but the products are generally obtained as highly cross-linked xerogels. To the best of our knowledge, this is the first example of the formation of well-defined cage-like oligomers. They can be a unique analogue of the silicate cage anions, leading to new chemistry and application. Moreover, the presence of $Si\text{–}O^-$ sites at the cage corners will allow further reactions to design a diverse class of hybrid materials.

The reaction in the **1**–EtOH–H_2O–TMAOH (1:20:20:3) system afforded a homogeneous solution, and gelation never occurred under this condition.† The ^{29}Si NMR spectrum of the solution exhibits two signals at −56.0 and −59.1 ppm with the relative intensity ratio of 1:2 (Fig. 1(a)). The signals are shifted upfield from that of **1** (−46 ppm), and are assigned to the T^2 units [$C\mathit{Si}(OSi)_2(OH \text{ or } O^-)$]. The quantitative analysis revealed the formation of a very high amount (>95%) of specific oligomers from **1**. Note that no signals corresponding to the Q units [Q^x, $\mathit{Si}(OSi)_x(OH)_{4-x}$], indicative of the cleavage of $Si\text{–}CH_2\text{–}Si$ linkages, are observable in the range of −70 to −115 ppm. The ^{13}C NMR spectrum of this solution (Fig. S1, ESI†) displays two signals (3.9, 4.3 ppm) assigned to the bridging methylene groups ($Si\text{–}\mathit{C}H_2\text{–}Si$).

Further characterization was carried out after trimethylsilylation of the T^2 units to stabilize against further condensation. The crystals of the silylated-derivative were isolated in high yield.† The ^{29}Si NMR spectrum shows two T^3 signals [$(C\mathit{Si}(OSi)_3)$, −61.1, −65.0 ppm] along with two M^1 signals [$C_3\mathit{Si}(OSi)$, 10.1, 10.6 ppm] due to trimethylsilyl groups with the intensity ratio of 1:2:1:2 (Fig. 1(b)), indicating the complete silylation without the degradation of the original siloxane structure. The FAB mass spectrum gave several peaks at around *m*/*z* 842 corresponding to the isotope pattern of $C_{21}H_{61}O_{12}Si_{12}$ accompanied by the lower *m*/*z* peaks due to the Si–Me and SiO–$SiMe_3$ fragmentations (Fig. S2, ESI†). These results indicate the formation of **1**-derived trimeric species where six Si atoms are capped by six trimethylsilyl groups.

There are two types of trimeric units consisting of only T^2 units (**2a** and **2b**), both of which have cage-like structures but the arrangements of $Si\text{–}CH_2\text{–}Si$ units are different. Based on the NMR data confirming the two environments of Si and C atoms, it is clear that **2a** was generated from **1**. The single-crystal X-ray analysis of the silylated-derivative also revealed the structure of **3a** (Fig. S3, ESI†).‡ The structure is analogous to the D3R silicate ($Si_6O_{15}{}^{6-}$),



Scheme 1 Formation of cage-like oligomers (**2a** and **2b**) from **1**, and silylation of **2a** with organochlorosilanes.

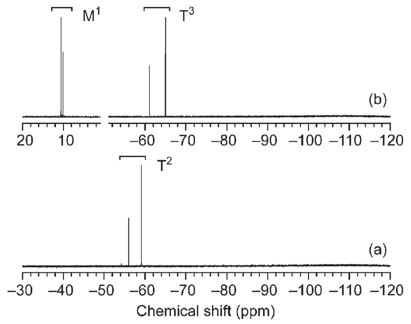


Fig. 1 Liquid-state ^{29}Si NMR spectra of (a) solution after 5 days of the reaction in the **1**–EtOH (10% ethanol-d_6)–H_2O–TMAOH (1:20:20:3) system and (b) trimethylsilylated-derivative (**3a**) dissolved in $CDCl_3$.

---

† Electronic supplementary information (ESI) available: Experimental section, spectroscopic data for **3a** and **3b**, crystallographic data for **3a**, and Figs. S1–S6. See http://www.rsc.org/suppdata/cc/b4/b411794h/

DOI: 10.1039/b411794h

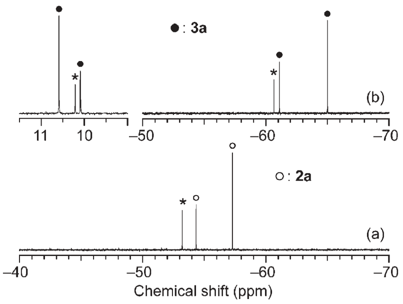


Fig. 2 Liquid-state ^{29}Si NMR spectra of (a) solution after 5 days of the reaction in the **1**–H_2O (10% D_2O)–TMAOH (1:80:3) system and (b) trimethylsilylated-derivatives dissolved in $CDCl_3$.

whereas the framework is distorted as a result of the partial replacement of bridging oxygen atoms by methylene groups. A similar cage-like oligomer derived from tetrafunctional precursor [$(EtO)_2MeSi–CH_2–SiMe(OEt)_2$] was mentioned in the literature.[10] The present result is unique in that cage-like oligomers are selectively formed from hexafunctional precursors. Also, by utilizing uncondensed Si–O$^-$ sites, **2a** can be functionalized by silylation with a variety of organochlorosilanes. For example, we obtained a silylated-derivative having vinyl groups (**3b**), which provides further chemical reactivity.

Interestingly, the presence of isomeric species (**2b**) was also confirmed when the reaction was performed in an aqueous solution (**1**–H_2O–TMAOH (1:80:3)). The ^{29}Si NMR spectrum (Fig. 2(a)) clearly shows a new T^2 signal at −53.2 ppm (*) which is observed with difficulty in Fig. 1(a).[11] The absence of T^1 units implies the formation of a cage-like oligomer rather than linear or cyclic species. After trimethylsilylation, the T^3 and M^1 signals appear with the intensity ratio of 1:1 (Fig. 2(b)). Although we could not separate this new species from the mixture of the silylated-derivatives, no trace of larger species (such as tetrameric units) was found by gel permeation chromatography (GPC) and FAB-MS (Figs. S4 and S5, ESI†). These results strongly suggest the coexistence of isomeric species (**2b**) consisting of six equivalent T^2 units. Attempt to obtain **2b** as the predominant species has not been achieved, which is possibly due to the lability of the relatively strained trisiloxane rings.[12]

Shea and Loy reported the formation of cyclic dimers at the initial stage of the hydrolysis and condensation of **1** in an acidic condition, but the reaction eventually led to gelation.[13] In addition, viscous polymers were formed by phase separation when NaOH was used instead of TMAOH in our system. We varied the TMAOH:**1** molar ratios in the **1**–EtOH–H_2O–TMAOH system, and found that **2a** was formed almost quantitatively when TMAOH:**1** $\geqslant$ 2:1 (TMAOH:Si $\geqslant$ 1:1). However, the yield considerably decreased as the ratio decreased to TMAOH:**1** = 1:1, and gelation occurred when TMAOH:**1** = 0.5:1. The above observations suggest that the interaction between TMA cations and Si–O$^-$ groups contributes to the formation and stabilization of cage structures. Recently, tetraalkylammonium cations were used as structure directing agents to prepare hybrid zeolite materials from **1** under hydrothermal conditions.[14] It appears that the role of TMA ions in our system is different because **2a** (or **2b**) does not exist as a building unit in the zeolite frameworks.

Earlier studies have shown that the D4R units ($Si_8O_{20}^{8-}$) are the predominant species in the silicate solution containing TMAOH.[7a] Actually, the D4R units were selectively formed in our system even when hexaethoxydisiloxane [$(EtO)_3Si–O–Si(OEt)_3$], which is similar to **1** but having a bridging oxygen atom, was used as the precursor. The preferential formation of the trimeric units (**2a** and **2b**) rather than tetrameric units from **1** should arise from the smaller Si–CH_2–Si angle compared with Si–O–Si angle. Molecular modeling with those angles of *ca.* 109 and 144°, respectively, and the O–Si–O (O–Si–C) angle of *ca.* 109° illustrates that the cage-like tetrameric units cannot be assembled without a large distortion of the framework. It is noteworthy that **1** forms the trimeric units even in the presence of tetraethyl-, tetrapropyl- or tetrabutyl-ammonium hydroxide instead of TMAOH (Fig. S6, ESI†). This is in contrast to the fact that the distribution of silicate species depends on the kind of tetraalkylammonium cations present in the solution.[7,15]

We have also examined the use of other precursors having longer alkylene bridges (–C_2H_4– and –C_3H_6–). However, cage-like oligomers were not formed by the reaction in the presence of TMA ions. This is presumably due to the flexibility of the bridging organic groups, which allows the formation of various species, including bicyclic dimers and cyclic monomers,[13] by inter- and intra-molecular condensation. Rigid organic groups seem to be essential for the formation of specific oligomers.

In conclusion, we have demonstrated the selective formation of novel cage-like oligomers, which are promising as versatile precursors to construct silica-based hybrid materials. Further work is underway to explore other types of hybrid cages with different structures and bridging organic groups.

The authors are grateful to Mr T. Goto and Ms H. Sunaga (MCCL, Waseda University) for X-ray analysis and MS measurement. The work was partially supported by a Grant-in-Aid for COE research, MEXT, Japan. A. S. thanks a financial support by a Grant-in-Aid for JSPS Fellows from MEXT.

Notes and references

‡ *Crystal data* for **3a** (recrystallized from acetonitrile): $C_{21}H_{60}O_{12}Si_{12}$, M_r = 841.77, primitive orthorhombic, space group *Pccn* (no. 56), a = 31.48(1), b = 11.622(5), c = 27.42(1) Å, U = 10029(7) Å^3, D_c = 1.115 g cm^{-3}, T = 298 K, Z = 8, μ(Cu–Kα) = 32.9 cm^{-1}, λ = 1.54187 Å, 62162 reflections measured, 5223 unique (R_{int} = 0.076); final R values: $R1$ = 0.068, $wR2$ = 0.172 ($I > 3\sigma(I)$); the data were collected on a Rigaku RAXIS RAPID imaging plate area detector following the standard procedure. The structure is not well refined because of poor diffraction in the high angle region. No hydrogens were refined, and three CH_3 groups on each trimethylsilyl group were refined over six positions with an occupancy of 0.5. The measurement 173 K was unsuccessful because of the deterioration of the single crystal. CCDC 250866. See http://www.rsc.org/suppdata/cc/b4/b411794h/ for crystallographic data in .cif or other electronic format.

1 B. Boury and R. J. P. Corriu, *Chem. Commun.*, 2002, 795.
2 A. Sayari and S. Hamoudi, *Chem. Mater.*, 2001, **13**, 3151.
3 P. G. Harrison, *J. Organomet. Chem.*, 1997, **542**, 141.
4 C. Sanchez, G. J. D. A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer and V. Cabuil, *Chem. Mater.*, 2001, **13**, 3061.
5 J. Choi, J. Harcup, A. F. Yee, Q. Zhu and R. M. Laine, *J. Am. Chem. Soc.*, 2001, **123**, 11420.
6 For example, see: (*a*) P. A. Agaskar, *Inorg. Chem.*, 1991, **30**, 2707; (*b*) F. J. Feher, D. A. Newman and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 1741; (*c*) A. R. Bassindale, Z. Liu, I. A. MacKinnon, P. G. Taylor, Y. Yang, M. E. Light, P. N. Horton and M. B. Hursthouse, *Dalton. Trans.*, 2003, 2945.
7 (*a*) D. Hoebbel, G. Garzó, G. Engelhardt and A. Vargha, *Z. Anorg. Allg. Chem.*, 1982, **494**, 31; (*b*) D. Hoebbel, G. Garzó, G. Engelhardt, R. Ebert, E. Lippmaa and M. Alla, *Z. Anorg. Allg. Chem.*, 1980, **465**, 15.
8 I. Hasegawa, *Polyhedron*, 1991, **10**, 1097.
9 (*a*) R. J. P. Corriu and D. Leclercq, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1420; (*b*) K. J. Shea and D. A. Loy, *Chem. Mater.*, 2001, **13**, 3306.
10 N. S. Nametkin, T. K. Islamov, L. E. Gusel'nikov and V. M. Vdovin, *Russ. Chem. Rev.*, 1972, **41**, 111.
11 The signals of **2a** in Fig. 2(a) (at −54.3 and −57.3 ppm) are slightly shifted downfield if compared with those in Fig. 1(a), which is due to the difference in solvent.
12 U. Damrau and H. C. Marsmann, *J. Non-Cryst. Solids*, 1994, **168**, 42.
13 K. J. Shea and D. A. Loy, *Acc. Chem. Res.*, 2001, **34**, 707.
14 K. Yamamoto, Y. Sakata, Y. Nohara, Y. Takahashi and T. Tatsumi, *Science*, 2003, **300**, 470.
15 D. Hoebbel, A. Vargha, G. Engelhardt and K. Újszászy, *Z. Anorg. Allg. Chem.*, 1984, **509**, 85.