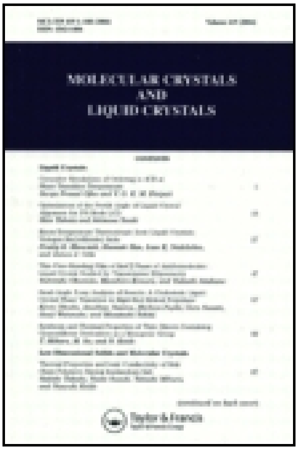

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Supramolecular Aggregates of Silanols and Solid-State Synthesis of Siloxanes

Masafumi Unno [a], Keisuke Takada [a], Yasuaki Kawaguchi [a] & Hideyuki Matsumoto [a]
[a] Department of Nano-Material Systems, Graduate School of Engineering, Gunma University, Kiryu, Gunma, Japan

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Supramolecular Aggregates of Silanols and Solid-State Synthesis of Siloxanes

Masafumi Unno
Keisuke Takada
Yasuaki Kawaguchi
Hideyuki Matsumoto
Department of Nano-Material Systems, Graduate School of Engineering,
Gunma University, Kiryu, Gunma, Japan

Cocrystallization of all-cis-tetraisopropylcyclotetrasiloxanetetraol and diisopropylsilanediol gave single crystals, which were proved to have a nano-size tube-like aggregate structure. Six molecules of the cyclic tetraol and four molecules of the diol form an asymmetric unit by means of hydrogen bonding. The structure and properties of the aggregates are discussed in detail, and also the possibility of solid-state synthesis of siloxanes is described.

Keywords: crystal structure; hydrogen bonding; nano-size tube; silanol; solid-state synthesis

INTRODUCTION

In recent years, we have reported reactions starting from silanols [1–5], and showed that all-*cis*-tetraisopropylcyclotetrasiloxanetetraol ([*i*-PrSiO(OH)]$_4$, **1**) was a versatile precursor of siloxanes of various structures. As shown in Figure 1, cage silsesquioxanes (octasilsesquioxane and hexasilsesquioxane) and ladder siloxanes (tricyclic and pentacyclic) were prepared. Regarding the structure of **1**, we have determined its configuration (all-*cis* form) by X-ray crystallography, and demonstrated its sphere-like packing structure on hydrogen bonding with water [3]. In 2000, we showed that the co-crystallization of

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Address correspondence to Hideyuki Matsumoto, Department of Nano-Material Systems, Graduate School of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan. E-mail: matumoto@chem.gunma-u.ac.jp

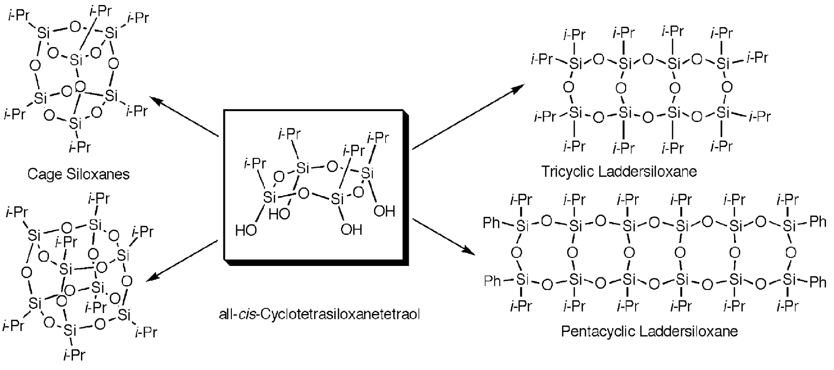


FIGURE 1 The structure of all-*cis*-cyclotetrasiloxanetetraol **1** and derived cage siloxane and ladder siloxane structures.

1 and diisopropylsilanediol **2** afforded the nano-size supramolecular aggregate **3** by means of hydrogen bonding [6]. As an extension, here we elaborate the structure and thermal properties of **3**, and explore the possibility of solid-state reaction yielding nano-sized siloxane tubes.

RESULTS AND DISCUSSION

Cyclic silanol **1** was prepared from isopropyltrichlorosilane in 22% yield [3], and silanediol **2** was obtained from diisopropyldichlorosilane in 81% by hydrolysis with aniline in water-ether. The co-crystallization was effected by slow evaporation from ether-hexane solution of both compounds. The X-ray crystallography was performed at –100°C, the structure was solved, and the space group determined to be $P2_1$. As shown in Figure 2, the asymmetric unit contains six molecules of **1** and four of the diol **2**. Each molecule was connected through hydrogen bonding, and the material composed an infinite length nano-size aggregate. Figure 3 indicates the top and side views of a space filling model. The structure resembles a micelle, however, the hydrophilic core (hydroxyl groups and siloxane oxygens) was surrounded by the hydrophobic isopropyl groups.

The melting point of **3** was 180–185°C, and higher than those of **1** (165–169°C) and **2** (106–109°C). The result of thermogravimetric analysis of **1–3** is shown in Figure 4. Tetraol **1** starts losing weight from 150°C, and completely sublimed at 578°C. Diol **2** lost all its weight at 149°C. On the other hand, the thermal profile of **3** is like an addition of **1** and **2**, except that the weight loss starts at 82°C, and is much

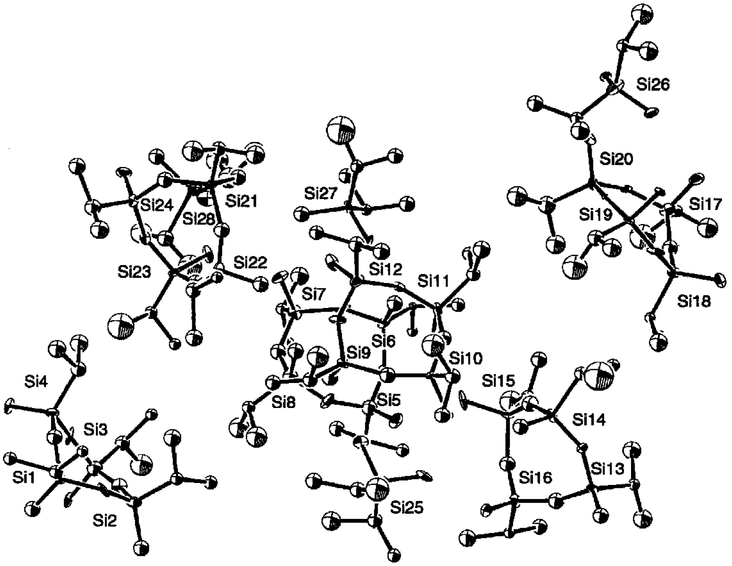


FIGURE 2 The asymmetric unit of the co-crystalline adduct **3** contains six molecules of **1** and four of diisopropylsilanediol **2**.

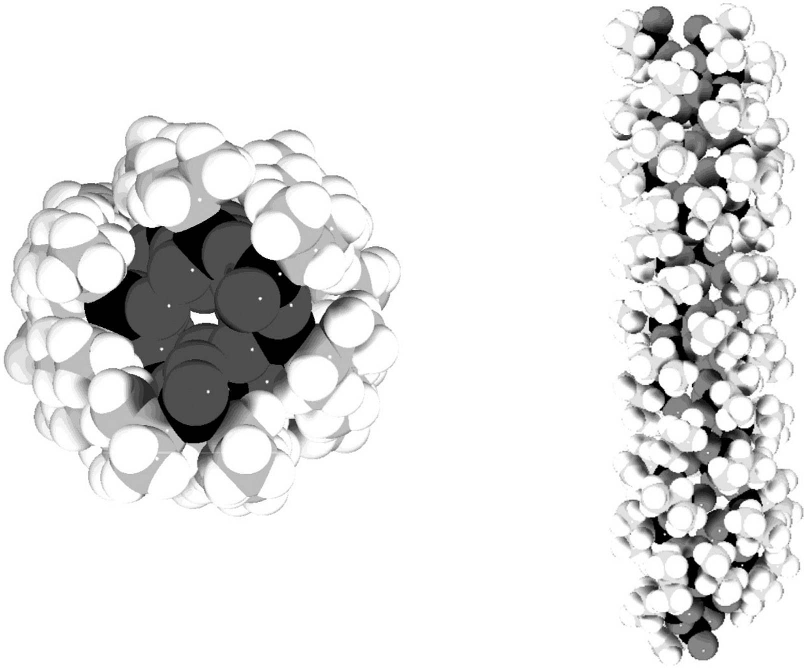


FIGURE 3 Top and side views of a space-filling model of the adduct **3**.

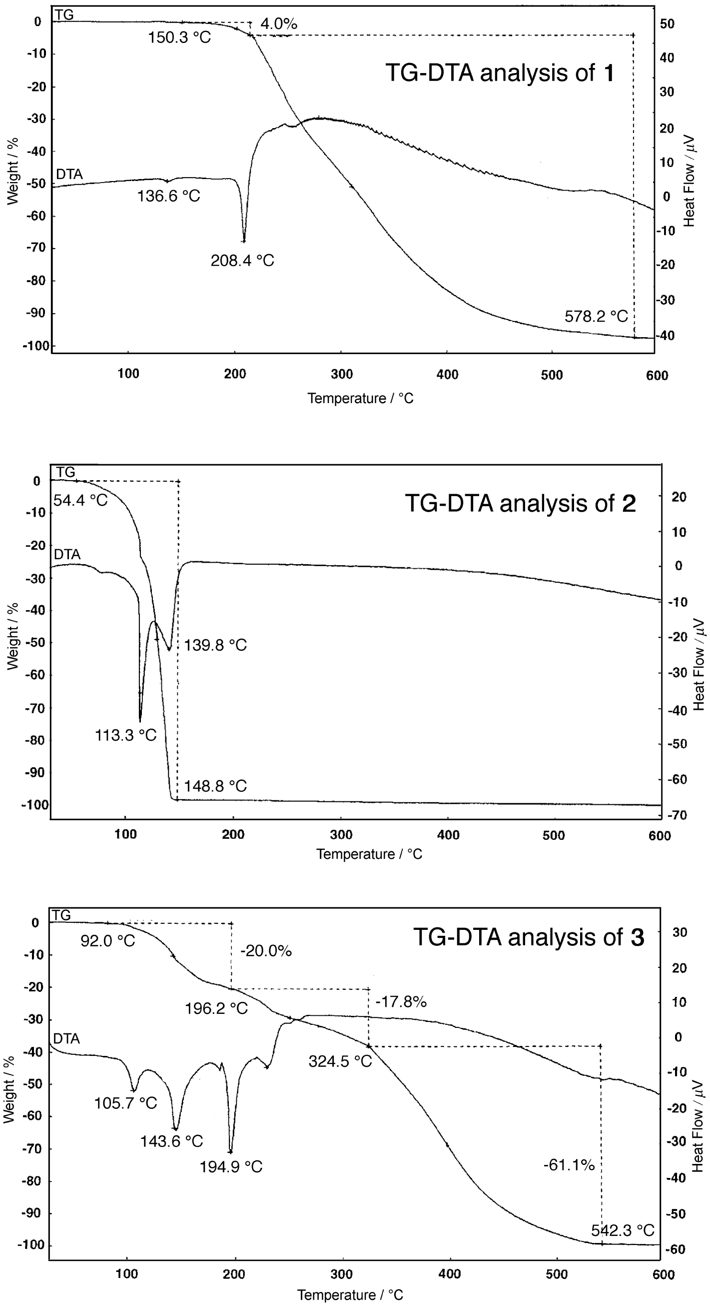
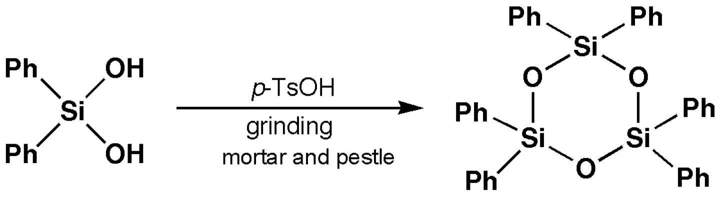


FIGURE 4 TG-DTA results for the compounds **1–3**.



40 min griding -> left for 1 h ->15 min grinding -> left for 3 h 49% yield

FIGURE 5 The dehydration of diphenyldisilane diol under solid state conditions.

higher than that of **2** (54°C). Unfortunately, no indication of dehydrative condensation in the solid state was observed. The calculated amount of weight loss when all the silanols condense is 9.3%, but the profile of **3** shows that one of the components (**2**) starts to sublime before condensation occurs.

Although the crystal is stable in air, dissolution in polar solvents cleaves the hydrogen bonding and the aggregate form is not observed any more. It is probable that the structure could be maintained in nonpolar solvents, but **3** was insoluble in such solvents. If we can transform **3** into a stable siloxane, the resulting material promises desirable properties as a nano-sized silicone tube. As the structure is not maintained in solution, transformation of **3** to a stable siloxane tube is only possible through solid-state reaction.

For solid-state dehydration of alcohols, Toda *et al.* reported the facile and high-yield transformation of aryl alcohols using a pestle and mortar in the presence of HCl gas, Cl_3CCOOH, or *p*-toluenesulfonic acid [7]. We applied this reaction to the dehydration of diphenylsilanediol as a model reaction. As shown in Figure 5, the target compound was obtained in 49% in the case of *p*-toluenesulfonic acid. Unfortunately, this reaction could not be performed for **3**, and resulted in the recovery of starting materials. All the model reactions including thermal reaction, microwave reaction, or under HCl gas gave no reactions. We are now seeking more effective dehydration reaction conditions.

REFERENCES

[1] Unno, M., Shamsul, B. A., Saito, H., & Matsumoto, H. (1996). Synthesis of hexasilsesquioxanes bearing bulky substituents: Hexakis(1,1,2-trimethylpropylsilsesquioxane) and hexakis(*tert*-butylsilsesquioxane). *Organometallics*, *15*, 2413–2414.

[2] Unno, M., Shamsul, B. A., Arai, M., Takada, K., Tanaka, R., & Matsumoto, H. (1999). Synthesis and characterization of cage and bicyclic silsesquioxanes via dehydration of silanols. *Appl. Organomet. Chem.*, *13*, 1–8.

[3] Unno, M., Takada, K., & Matsumoto, H. (1998). Synthesis, structure, and reaction of the tetrahydroxycyclotetrasiloxane $[(i\text{-Pr})(OH)SiO]_4$. *Chem. Lett.*, 489–490.

[4] Unno, M., Suto, A., Takada, K., & Matsumoto, H. (2000). Synthesis of ladder and cage silsesquioxanes from 1,2,3,4-tetrahydroxycyclotetrasiloxane. Bull. *Chem. Soc. Jpn.*, *73*, 215–220.

[5] Unno, M., Suto, A., & Matsumoto, H. (2002). Pentacyclic laddersiloxane. *J. Am. Chem. Soc.*, *124*, 1574–1575.

[6] Unno, M., Takada, K., & Matsumoto, H. (2000). Formation of supramolecule by assembling of two different silanols. *Chem. Lett.*, 242–243.

[7] Toda, F., Takumi, H., & Akehi, M. (1990). Efficient solid-state reactions of alcohols: dehydration, rearrangement, and substitution. *Chem. Commun.*, 1270–1271.