Formation of Incompletely Condensed Oligosilsesquioxanes by Hydrolysis of Completely Condensed POSS via Reshuffling

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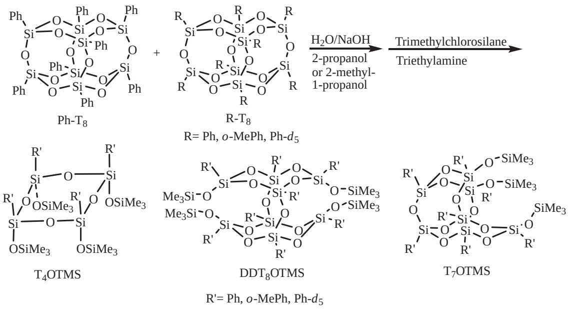
Cyclic 1,3,5,7-tetrakis(trimethylsilyl)tetraphenyltetrasilsesquioxane (T_4OTMS), 3,7,14-tris(trimethylsilyl)heptaphenyltricyclo[7.3.3.1^{5,11}]heptasilsesquioxane (T_7OTMS), and 5,11,14,17-tetrakis(trimethylsilyl)octaphenyltetracyclo[7.3.3.3^{3,7}]octasilsesquioxane (DDT_8OTMS) were found to be formed by the hydrolysis of completely condensed polyhedral oligomeric silsesquioxanes (POSS) followed by trimethylsilyl (TMS)-capping. The reaction was shown to be a reshuffling process by the scrambling of substitutents in co-hydrolysis of differently substituted POSS.

Incompletely condensed silsesquioxane frameworks play an important role as useful building blocks for silsesquioxane-containing polymers,[1] silica-supported catalysts, network solids,[2] etc. In order to synthesize incompletely condensed POSS conveniently, Feher and co-workers have attempted the controlled cleavage of completely condensed POSS frameworks under both acidic and basic conditions,[3] and the formation of T_7 structure was reported in the presence of tetraethylammonium hydroxide. Stimulated by this fact, we studied the cleavage of completely condensed octaphenyloctasilsesquioxane (Ph-T_8) under more strongly basic conditions. Here, we would like to report a new procedure to form cyclic tetramer, incompletely condensed double deck POSS derivatives, through framework rearrangement of Ph-T_8.

Apparent reaction paths are shown in Scheme 1. The synthetic results are summarized in Table 1.

When Ph-T_8 was hydrolyzed with water and sodium hydroxide (Ph-T_8:H_2O:NaOH = 1:2:4 in molar ratio) in 2-propanol at room temperature for 40 h, a cyclic tetramer (T_4OTMS) with all cis configuration was produced as the major component in the soluble portion, proven by treatment with trimethylchlorosilane (No. 1 in Table 1).[4,5] It is worthwhile to comment that 1-[bis(trimethylsiloxy)]phenylsiloxy-3,5,7-tris(trimethylsiloxy)-1,3,5,7-tetraphenylcyclosiloxane was observed among the hydrolysis products from Ph-T_8 followed by TMS-capping at rt, although in small amount.[4] This fact may suggest the slower cleavage of silicon–oxygen bonds in the formed rings through the initial cleavage of the T_8 cage.



Scheme 1. Formation of incompletely condensed silsesquioxane derivatives via the hydrolysis of completely condensed POSS followed by TMS-capping.

A double-deck POSS, DDT_8OTMS, was obtained in high yield, when the hydrolysis was carried out in refluxing 2-propanol or at 90 °C in 2-methyl-1-propanol for 24 h (Nos. 2 and 3 in Table 1).[4,6]

When the ratio of raw materials (Ph-T_8:H_2O:NaOH) was changed from 1:2:4 (molar ratio) to 1:1:2 (molar ratio), as shown in Table 1 (No. 4), 3,7,14-tris(trimethylsilyl)heptaphenyltricyclo-[7.3.3.1^{5,11}]heptasilsesquioxane (T_7OTMS) was the main product.[4,5]

Consequently, hydrolysis of Ph-T_8 by sodium hydroxide in water–alcohol solvents was a selective method to obtain cyclic tetramer, DDT_8, and T_7 frameworks depending on the reaction temperature and the ratio of raw materials. Comparing to our previous report,[6] although the yield of T_4 and T_7 was lower, a higher yield was obtained for the formation of double deck T_8 from cage T_8.

In order to find a reasonable mechanism of the hydrolysis illustrated above, co-hydrolysis of Ph-T_8 with octa(phenyl-d_5)-octasilsesquioxane (Ph-d_5-T_8) and octa(*o*-methylphenyl)octasilsesquioxane (*o*-MePh-T_8) was carried out. Interestingly, scrambling of functional groups was found. As shown in Table 1 (No. 5), when co-hydrolysis of Ph-T_8 and Ph-d_5-T_8 was carried

Table 1. Products in the hydrolysis of completely condensed POSS followed by TMS-capping[a]

No.	R	Solvent	Temperature/°C	Time/h	Products	Yield/%
1	Ph[b]	2-propanol	rt	40	T_4OTMS	24
2	Ph[b]	2-propanol	Reflux[c]	24	DDT_8OTMS	72
3	Ph[b]	2-methyl-1-propanol	90	24	DDT_8OTMS	69
4	Ph[d]	2-propanol	Reflux[c]	24	T_7OTMS	44
5	Ph-d_5[e]	2-propanol	Reflux[c]	24	DDT_8OTMS	≈36[f]
					T_7OTMS	≈18[f]
6	*o*-MePh[g]	2-propanol	Reflux[c]	24	T_7OTMS	≈42[f]
7	Ph-d_5[h]	2-propanol	rt	40	Only T_4OTMS was detected with MALDI-TOFMS.	

[a]Structures are shown in Scheme 1. [b]Ph-T_8:H_2O:NaOH = 1:2:4 (molar ratio), Ph-T_8/solvent = 1 mmol/6 mL. [c]The temperature of the oil bath was about 90 °C, at which the reaction solution was kept at reflux under 1 standard atmosphere. [d]Ph-T_8:H_2O:NaOH = 1:1:2 (molar ratio), Ph-T_8/solvent = 1 mmol/10 mL. [e]Ph-T_8:Ph-d_5-T_8:H_2O:NaOH = 1:1:4:8 (molar ratio), (Ph-T_8 + Ph-d_5-T_8)/solvent = 1 mmol/25 mL. [f]The yield was estimated with average molecular weight based on MALDI-TOFMS data, because the products have a molecular weight distribution. [g]Ph-T_8:*o*-MePh-T_8:H_2O:NaOH = 1:1:4:8 (molar ratio), (Ph-T_8 + *o*-MePh-T_8)/solvent = 1 mmol/9 mL. [h]Ph-T_8:Ph-d_5-T_8:H_2O:NaOH = 1:1:4:8 (molar ratio), (Ph-T_8 + Ph-d_5-T_8)/solvent = 1 mmol/22 mL.

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Table 2. MALDI-TOFMS data for T_7OTMS, DDT_8OTMS, and T_4OTMS obtained from co-hydrolysis of completely condensed POSS followed by TMS-capping

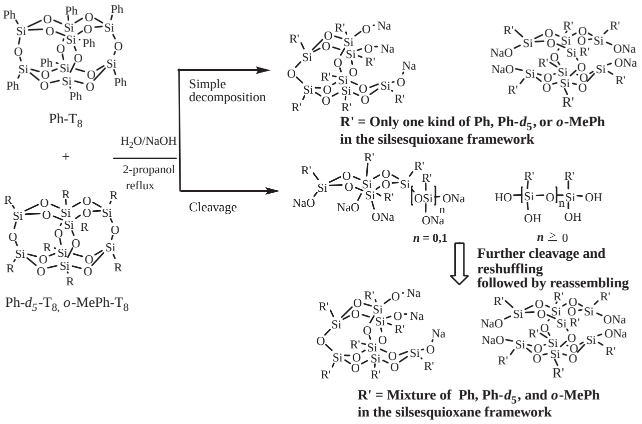
Compd	Ph/R	Relative[a] intensity/%	m/z [M + Na]$^+$ (Found)	m/z [M + Na]$^+$ (Calcd)
T_7OTMS[b] R = Ph-d_5	6/1	25	1174.61	1174.21
	5/2	63	1180.15	1179.25
	4/3	100	1185.22	1184.28
	3/4	99	1189.26	1189.31
	2/5	64	1195.16	1194.34
	1/6	34	1199.09	1199.37
DDT_8OTMS[b] R = Ph-d_5	7/1	11	1384.50	1384.27
	6/2	21	1389.99	1389.30
	5/3	40	1394.82	1394.33
	4/4	45	1399.65	1399.36
	3/5	41	1403.99	1404.39
	2/6	26	1409.81	1409.42
	1/7	11	1415.48	1414.46
T_7OTMS[c] R = o-MePh	6/1	22	1184.49	1183.20
	5/2	56	1197.51	1197.21
	4/3	99	1212.47	1211.23
	3/4	100	1226.51	1225.25
	2/5	58	1240.53	1239.26
	1/6	22	1254.61	1253.28
T_4OTMS[d] R = Ph-d_5	4/0	22	863.16	863.20
	3/1	44	867.84	868.23
	2/2	96	872.82	873.27
	1/3	100	877.91	878.30
	0/4	60	883.81	883.33

[a] 100% for the highest peak. [b] Obtained via co-hydrolysis of Ph-T_8 and Ph-d_5-T_8 under refluxing condition of 2-propanol. [c] Obtained via co-hydrolysis of Ph-T_8 and o-MePh-T_8 under refluxing condition of 2-propanol. [d] Obtained via co-hydrolysis of Ph-T_8 and Ph-d_5-T_8 at rt.

out, not only DDT_8OTMS but also T_7OTMS was formed. The molar ratio of DDT_8OTMS to T_7OTMS, estimated from ^{29}Si NMR, was about 1.5 to 1. The weight ratio after column chromatography was 2.33/1.[4] Co-hydrolysis of Ph-T_8 and octa(o-methylphenyl)octasilsesquioxane (o-MePh-T_8) under the same condition gave only T_7OTMS as the product (No. 6 in Table 1).[4] Steric factors seem also to be operating in the hydrolysis of completely condensed POSS. In ^{29}Si NMR, peaks of silsesquioxane frameworks of both T_7OTMS and DDT_8OTMS were separated into two different chemical shifts.[4] The reason is that phenyl and phenyl-d_5 substituents were randomly distributed in T_7 and the double-deck frameworks, and that the silicon atoms linked to phenyl and phenyl-d_5 substituents have only a little different electronic effect. More quantitative data were obtained by MALDI-TOFMS. Deuterated substituents were distributed randomly in both T_7OTMS and DDT_8OTMS, as shown in Table 2.

A similar phenomenon was also found in the co-hydrolysis of Ph-T_8 and o-MePh-T_8. The complexity of ^{29}Si NMR of the product T_7OTMS suggested random distribution of phenyl and o-methylphenyl in T_7OTMS. MALDI-TOFMS clearly indicated that each T_7OTMS component has different phenyl/o-methylphenyl ratio, as listed in Table 2.[4] These statistical ratios suggested random distribution of phenyl and o-methylphenyl substituents in T_7OTMS. Rikowski and Marsmann also reported a similar partial scrambling of POSS derivatives in the formation of deca- and dodecasilsesquioxane cages from cage octasilsesquioxanes.[7]

As shown in Table 2, the scrambling of substituents occurred even at room temperature for T_4OTMS, although not as extensive as that for DDT_8OTMS and T_7OTMS at refluxing temperature of the solvent.[4]



Scheme 2. Expected co-hydrolysis products in two different reaction mechanisms.

Based on these facts, reaction mechanism was considered. If the hydrolysis of cage T_8 is a simple decomposition process, the frameworks of T_7OTMS and DDT_8OTMS should consist of only one kind of the same substitutent (upper case in Scheme 2), but this is not the case. Random distribution of substituents in the products in the co-hydrolysis of Ph-T_8 with Ph-d_5-T_8 and o-MePh-T_8 provides strong evidence for the hydrolysis of these POSS as a reshuffling process, by which completely condensed POSS decomposed into smaller fragments, and then reassembled to form double-deck, and T_7 structures.

In summary, incompletely condensed oligosilsesquioxane frameworks with controlled structure, including cyclic tetramer, T_7, and DDT_8, were prepared by the hydrolysis of completely condensed POSS selectively with the modification of reaction conditions. The hydrolysis reaction was proved be a reshuffling process. This process provides opportunities for the preparation of a variety of new incompletely condensed and functionalized POSS from the T_8 framework.

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References and Notes

1 For examples, see: a) S. Wu, T. Hayakawa, R. Kikuchi, S. J. Grunzinger, M. Kakimoto, H. Oikawa, *Macromolecules* **2007**, *40*, 5698. b) M. Seino, T. Hayakawa, Y. Ishida, M. Kakimoto, K. Watanabe, H. Oikawa, *Macromolecules* **2006**, *39*, 3473. c) K. Ohno, S. Sugiyama, K. Koh, Y. Tsujii, T. Fukuda, M. Yamahiro, H. Oikawa, Y. Yamamoto, N. Ootake, K. Watanabe, *Macromolecules* **2004**, *37*, 8517.

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3 a) F. J. Feher, D. Soulivong, *Mater. Res. Soc. Symp. Proc.* **1999**, *576*, 111. b) F. J. Feher, R. Terroba, J. W. Ziller, *Chem. Commun.* **1999**, 2309.

4 See Supporting Information for experimental details and spectral data of the products. The material is available electronically on the CSJ-Journal website, http://www.csj.jp/journals/chem-lett/.

5 Cyclic tetraphenylsilsesquoxanetetraol (T_4OH), and heptaphenylsilsesquioxanetriol (T_7OH) might be easily prepared from cyclic tetraphenylsilsesquioxanetetraol tetrasodium salt (T_4ONa), and heptaphenylsilsesquioxanetriol trisodium salt (T_7ONa) by neutralization, respectively. In this research, we focused on the formation of cyclic tetramer and POSS frameworks. So, TMS-capping reaction was carried out in order to characterize the products conveniently.

6 Double-deck octaphenylsilsesquioxanetetraol (DDT_8OH), a useful building block for higher ordered structures, can be prepared from double-deck octaphenylsilsesquioxanetetraol tetrasodium salt (DDT_8ONa) easily by neutralization with acetic acid. This process has been reported: D. W. Lee, Y. Kawakami, *Polym. J.* **2007**, *39*, 230, so, the neutralization of DDT_8ONa was not repeated, meanwhile TMS-capping reaction was carried out in order to characterize the product conveniently.

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