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Research Article

Nonacyclic Ladder Silsesquioxanes and Spectral Features of Ladder Polysilsesquioxanes

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Laddersiloxanes, that is, ladder silsesquioxanes with defined structures, could be obtained by stepwise synthesis starting from cyclic silanols. These compounds were shown to have high thermal stability. As an extension of the previous work, the first nonacyclic ladder silsesquioxanes were synthesized by the reaction of bicyclic silanol with tricyclic tetrachloride, which were obtained from cyclic silanols. The structure was confirmed by spectral measurements, and the spectral features of a series of ladder polysilsesquioxanes with determined structures were analyzed.

1. Introduction

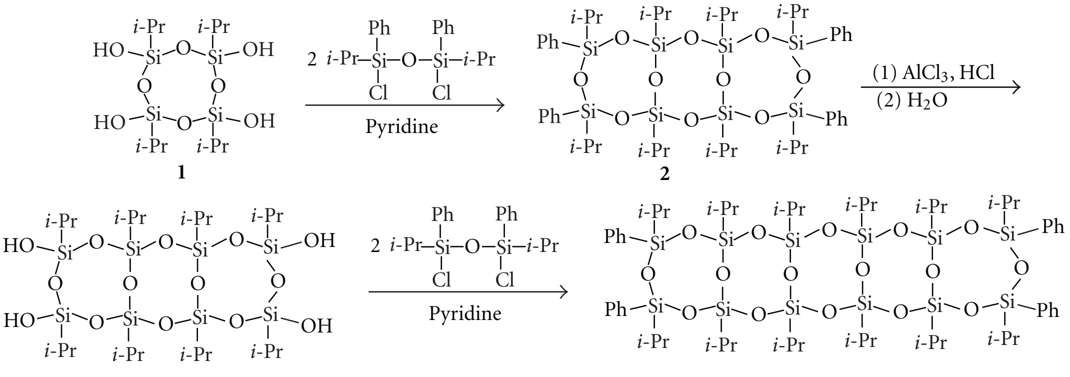
Recently, the interest in ladder silsesquioxanes has been growing mainly because of their high thermal stability and their application to functional materials [1–3]. To study the relationship between the structure and properties, we prepared ladder silsesquioxanes, determined their structures, and investigated the properties. We referred to these ladder silsesquioxanes as "laddersiloxanes," and we reported the syntheses and crystallographic analysis of tricyclic laddersiloxanes [4, 5]; pentacyclic laddersiloxanes [6]; bi-, tri-, tetra-, and pentacyclic laddersiloxanes with an all *anti* conformation [7]; extendible pentacyclic laddersiloxanes [8] and heptacyclic laddersiloxanes by a stereocontrolled approach [9]. As an extension, herein, we report the synthesis of the first nonacyclic ladder silsesquioxanes.

2. Experiments

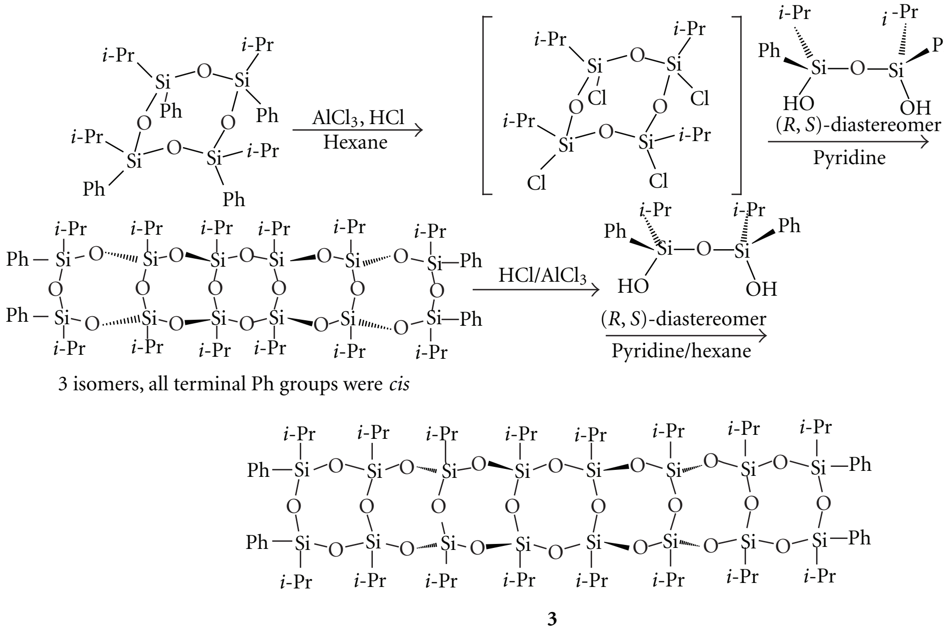
Preparative recycle-type high-performance liquid chromatography (HPLC) was carried out by using a JAI LC-908 HPLC with a Chemco 7-ODS-H column (20 × 250 mm). The Fourier-transform nuclear magnetic resonance (NMR) spectra were obtained by using a JEOL model Λ-500 (^{1}H NMR at 500.00 MHz, ^{13}C NMR at 125.65 MHz, and ^{29}Si NMR at 99.25 MHz). The chemical shifts were reported as δ units (ppm) relative to $SiMe_4$, and the residual solvent peaks were considered as the standard. Electron impact mass spectrometry was performed with a JEOL JMS-DX302. The infrared spectra were measured with a Shimadzu FTIR-8700.

*2.1. Preparation of Bicyclic Ladder Silanol (**4**).* A solution of (i-PrPhSiCl)$_2$O [6] (1.02 g, 2.66 mmol) in pyridine (8 mL) was added dropwise to [i-Pr(OH)SiO]$_4$ (1.02 g, 2.45 mmol) [10–12] in pyridine (8 mL) for 3 h at 0°C. The mixture was stirred for an additional 20 min at 0°C. The reaction mixture was added to saturated aqueous NH_4Cl and hexane, and two phases were separated. The aqueous phase was extracted with hexane. The organic phase was then washed with saturated aqueous NH_4Cl, then dried over anhydrous magnesium sulfate, and concentrated. The crude product was separated by dry column chromatography (eluent: hexane/Et_2O = 9 : 1), followed by the separation using recycle-type HPLC (eluent: MeOH/THF = 9 : 1) to give bicyclic ladder silanols (**4**, 1.00 g, 56%) (isomeric mixture). They were identified by the comparison with authentic sample [4, 5].

2.2. Reaction of Tricyclic Laddersiloxanes Tetrachloride with Bicyclic Ladder Silanols. A solution of bicyclic ladder silanols



Scheme 1: Synthesis of pentacyclic laddersiloxanes.

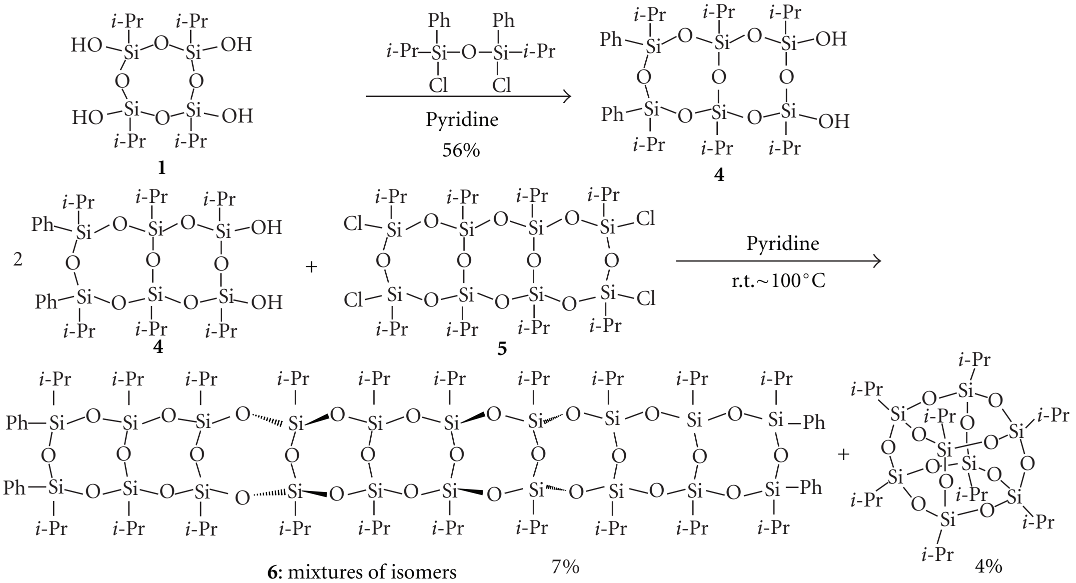


Scheme 2: Synthesis of heptacyclic laddersiloxanes.

(**4**) (1.00 g, 1.38 mmol) in pyridine (4 mL) was added dropwise to a solution of tetrachloro-tricyclic laddersiloxanes (**5**) [6] (0.552 g, 0.600 mmol) in pyridine (6 mL) for 13 min at room temperature. The mixture was stirred for 5 d at 100°C. The reaction mixture was added to saturated aqueous NH_4Cl and hexane, and two phases were separated. The aqueous phase was extracted with hexane. The combined organic phase was washed with saturated aqueous NH_4Cl, then dried over anhydrous magnesium sulfate, and concentrated. Ethanol was added to the concentrate, and the resulting $(i\text{-PrSiO}_{1.5})_8$ (26 mg, 6%) was obtained by filtration. The filtrate was separated by dry column chromatography (eluent: hexane/Et_2O = 9 : 1), followed by separation with recycle-type gel permeation chromatography (GPC) (eluent: THF) to give nonacyclic ladder silsesquioxanes (isomeric mixture) (**6**) (98 mg, 7%). **6**: MS (70 eV) *m/z* (%) 2134 (M^+-*i*-Pr, 5), 28 (100). IR (NaCl) ν 3072, 3051, 2947, 2895, 2868, 1593, 1466, 1429, 1387, 1366, 1259, 1115, 1034, 999, 920, 889, 719, 702 cm^{-1}.

3. Results and Discussions

3.1. Synthesis of Nonacyclic Ladder Silsesquioxanes. Our strategy for constructing a real ladder structure is based on the reaction of cyclotetrasiloxane units [10–12]. Recently, Gunji's group reported the synthesis of ladder polysilsesquioxane starting from cyclotetrasiloxane units [13], showing that this unit is essential to obtain the real ladder structure. As can be seen from Scheme 1, all *cis*-cyclotetrasiloxanetetraol **1** was treated with dichlorodisiloxane to give tricyclic laddersiloxanes **2**. Dephenylchlorination that was followed by hydrolysis afforded tricyclic tetraols, and then, a similar procedure could be applied again to extend ladder [6]. The obtained pentacyclic laddersiloxanes (mixture of isomers) were isolated by recycle-type reverse-phase HPLC, and the structure of one of the isomers was determined by X-ray crystallography. In this synthesis, tricyclic laddersiloxanes **2** were obtained in a good yield (85%), but the yield of pentacyclic laddersiloxane was not satisfactory (47%,



Scheme 3: Synthesis of nonacyclic ladder silsesquioxanes.

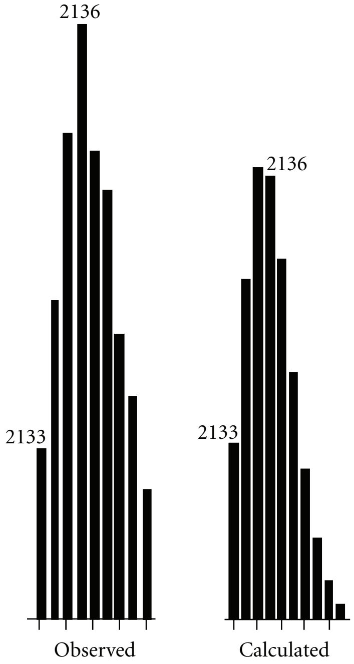


Figure 1: Observed and calculated mass spectra of nonacyclic ladder silsesquioxanes **6.**

mixture of five stereoisomers). This can be attributed to the generation of disadaptive isomers. Additional rings can be formed when the terminal hydroxyl groups are in the *cis* position. However, when two hydroxyl groups are in *trans* position, laddersiloxanes cannot be obtained. This explains why the yield of pentacyclic laddersiloxanes was not high.

Therefore, in the case of heptacyclic laddersiloxanes **3**, we separated and utilized (1R,3S)-disiloxanediol in order to obtain extendible products [8] (Scheme 2). By the reaction

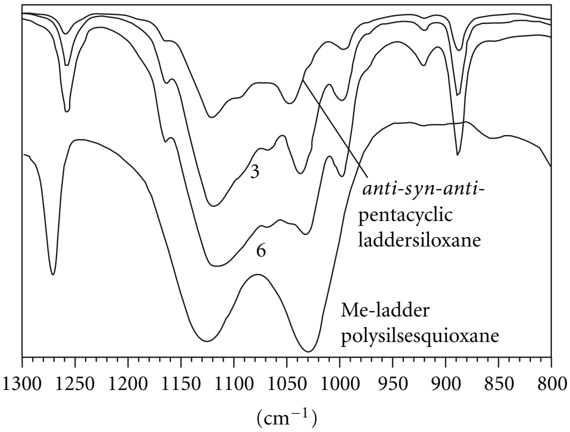


Figure 2: IR spectra of pentacyclic, heptacyclic, nonacyclic laddersiloxanes and ladder polysilsesquioxanes.

with (R,S)-disiloxanediol, only *cis*-diphenyl pentacyclic laddersiloxanes were obtained. These laddersiloxanes enabled us to obtain **3**.

Although the obtained heptacyclic laddersiloxanes **3** could be theoretically extendible, synthesis of nonacyclic laddersiloxanes from heptacyclic laddersiloxanes was unsuccessful because of the lack of enough supply of starting heptacyclic laddersiloxanes. Therefore, we devised alternative approach.

During the preparation of tricyclic laddersiloxane **2**, we observed the generation of bicyclic diol **4** as a by-product. To obtain **4** in a higher yield, we treated **1** with 1 equiv. of dichlorodisiloxane. As shown in Scheme 3, the desired diol **4** was obtained in 56% yield. When we reacted **4** with tricyclic tetrachloride **5**, which was prepared in the synthesis of pentacyclic laddersiloxanes [6], target nonacyclic ladder silsesquioxanes **6** were obtained as a mixture of isomers

Table 1: ^{29}Si NMR chemical shift of laddersiloxanes.

Compounds	^{29}Si NMR chemical shift/ppm
syn-Tricyclic laddersiloxane [4, 5]	−67.2
anti-Tricyclic laddersiloxane [4, 5]	−66.8
All *anti*-Pentacyclic laddersiloxane [7]	−65.8, −65.2
anti-syn-syn-Pentacyclic laddersiloxane [6]	−66.5, −65.9
Heptacyclic laddersiloxane (isomeric mixture) **3** [8]	−66.2 to −64.9
Nonacyclic ladder silsesquioxanes (isomeric mixture) **6**	−66.5 to −65.5
Methyl ladder polysilsesquioxane (solid state) [9]	−64.5

(7%) with octasilsesquioxane (6%). As in the case of heptacyclic laddersiloxanes, nonacyclic ladder silsesquioxanes were obtained as a viscous oil, and X-ray crystallographic analysis was impossible. Therefore, we determined the structure of **6** by spectroscopic analysis.

The ^{29}Si NMR spectrum of **6** in $CDCl_3$ showed multiple peaks between −66.52 and −65.45 ppm and between −34.53 and −32.80 ppm. The peaks around −65 ppm were attributed to the internal silicon atom, and those around –34 ppm were attributed to the terminal Si(–Ph) atom. The chemical shifts of silicon (T) atoms in laddersiloxanes, whose structures were determined by X-ray analysis, are summarized in Table 1. The ^{29}Si NMR value of **6** was in good agreement with those of other laddersiloxanes. In addition, the mass spectrum showed a peak at 2133 (M^+–C_3H_6), and the isotope pattern was similar to the calculated one (Figure 1). From these results, the obtained product was identified as a nonacyclic ladder silsesquioxanes.

3.2. Spectral Features of Ladder Silsesquioxanes. The ^{29}Si NMR chemical shifts of internal silicon atoms of laddersiloxanes are summarized in Table 1. The results indicate that ^{29}Si NMR peaks of laddersiloxanes and ladder polysilsesquioxanes are observed in a narrow area and are independent of the number of rings, stereostructures, and terminal substituents.

The IR spectra are very useful for the characterization of ladder silsesquioxanes. As Yoon's group has shown in their theoretical IR studies [14], ladder silsesquioxanes are characterized by two peaks around 1150 cm^{-1} and 1050 cm^{-1}, while IR spectra of cage silsesquioxanes do not have a peak at 1050 cm^{-1} [14]. As shown in Figure 2, two peaks were detected in that region for all laddersiloxanes. Because heptacyclic and nonacyclic laddersiloxanes are a mixture of stereoisomers, these two peaks are rather broad and are comprised of several peaks. On the other hand, absorption peaks of ladder polysilsesquioxanes were sharp and symmetrical, showing the highly organized structure.

Acknowledgments

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References

[1] S. S. Choi, A. S. Lee, H. S. Lee et al., "Synthesis and characterization of UV-curable ladder-like polysilsesquioxane," *Journal of Polymer Science Part A*, vol. 49, no. 23, pp. 5012–5018, 2011.

[2] M. Handke, B. Handke, A. Kowalewska, and W. Jastrzebski, "New polysilsesquioxane materials of ladder-like structure," *Journal of Molecular Structure*, vol. 924–926, pp. 254–263, 2009.

[3] H. Seki, N. Abe, Y. Abe, and T. Gunji, "Synthesis and structure of syn,anti,syn-pentacyclic ladder oligomethylsilsesquioxane," *Chemistry Letters*, vol. 40, no. 7, pp. 722–723, 2011.

[4] M. Unno, B. A. Shamsul, M. Arai, K. Takada, R. Tanaka, and H. Matsumoto, "Synthesis and characterization of cage and bicyclic silsesquioxanes via dehydration of silanols," *Applied Organometallic Chemistry*, vol. 13, no. 4, pp. 303–310, 1999.

[5] M. Unno, A. Suto, K. Takada, and H. Matsumoto, "Synthesis of ladder and cage silsesquioxanes from 1,2,3,4-tetrahydroxycyclotetrasiloxane," *Bulletin of the Chemical Society of Japan*, vol. 73, no. 1, pp. 215–220, 2000.

[6] M. Unno, A. Suto, and H. Matsumoto, "Pentacyclic laddersiloxane," *Journal of the American Chemical Society*, vol. 124, no. 8, pp. 1574–1575, 2002.

[7] M. Unno, R. Tanaka, S. Tanaka, T. Takeuchi, S. Kyushin, and H. Matsumoto, "Oligocyclic ladder polysiloxanes: alternative synthesis by oxidation," *Organometallics*, vol. 24, no. 4, pp. 765–768, 2005.

[8] M. Unno, T. Matsumoto, and H. Matsumoto, "Synthesis of laddersiloxanes by novel stereocontrolled approach," *Journal of Organometallic Chemistry*, vol. 692, no. 1-3, pp. 307–312, 2007.

[9] S. Chang, T. Matsumoto, H. Matsumoto, and M. Unno, "Synthesis and characterization of heptacyclic laddersiloxanes and ladder polysilsesquioxane," *Applied Organometallic Chemistry*, vol. 24, no. 3, pp. 241–246, 2010.

[10] M. Unno, K. Takada, and H. Matsumoto, "Synthesis, structure, and reaction of the tetrahydroxycyclotetrasiloxane, $[(i\text{-}Pr)(OH)SiO]_4$," *Chemistry Letters*, no. 6, pp. 489–490, 1998.

[11] M. Unno, K. Takada, and H. Matsumoto, "Formation of supermolecule by assembling of two different silanols," *Chemistry Letters*, no. 3, pp. 242–243, 2000.

[12] M. Unno, Y. Kawaguchi, Y. Kishimoto, and H. Matsumoto, "Stereoisomers of 1,3,5,7-tetrahydroxy-1,3,5,7-tetraisopropylcyclotetrasiloxane: synthesis and structures in the crystal," *Journal of the American Chemical Society*, vol. 127, no. 7, pp. 2256–2263, 2005.

[13] H. Seki, T. Kajiwara, Y. Abe, and T. Gunji, "Synthesis and structure of ladder polymethylsilsesquioxanes from silafunctionalized cyclotetrasiloxanes," *Journal of Organometallic Chemistry*, vol. 695, no. 9, pp. 1363–1369, 2010.

[14] E. S. Park, H. W. Ro, C. V. Nguyen, R. L. Jaffe, and D. Y. R. Yoon, "Infrared spectroscopy study of microstructures of poly(silsesquioxane)s," *Chemistry of Materials*, vol. 20, no. 4, pp. 1548–1554, 2008.