Regulation of Main-Chain Conformation of Permethyldecasilane by Complexation with γ-Cyclodextrin

Kenkichi Sakamoto,* Takehiko Naruoka, and Mitsuo Kira*
Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578

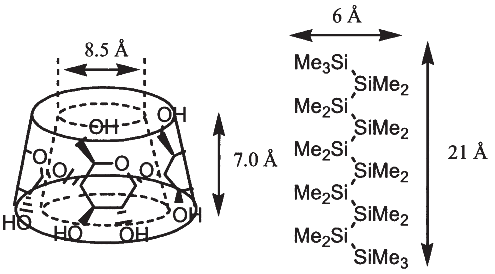
(Received January 17, 2003; CL-030051)

An absorption and emission spectroscopic study of an inclusion complex of permethyldecasilane (**1**) with γ-cyclodextrin in water has shown that the silicon main chain of **1** has an all-trans rod-like conformation in the hydrophobic cavities of γ-cyclodextrin at room temperature.

Linear-chain polysilane polymers whose main chains are constructed by catenated silicon atoms are known to show unique optoelectronic properties such as remarkable thermochromic behavior.[1] For instance, while poly(dihexylsilylene) exhibits an intense absorption band at 315 nm at 25 °C, upon cooling below ca. −30 °C, the absorption bandwidth becomes much narrower and the maximum shifts to 355 nm.[2] Similar thermochromic behavior has been observed for long-chain linear oligosilanes.[3,4] The origin of the thermochromism and other chromic behavior of linear polysilanes and long-chain linear oligosilanes is usually ascribed to the conformational transition of the silicon main chain from a random coil to a rod form.[5] Recent studies of the optical properties of conformationally fixed oligosilanes by Michl et al.[6] and Tamao et al.[7] have presented a more detailed description of the relationship between the main-chain conformation of linear oligosilanes and the optical properties.

Very recently, Harada et al. reported the synthesis and structure of inclusion complexes of permethylpolysilanes with cyclodextrins.[8,9] Here we report the absorption and emission spectroscopic behavior of an inclusion complex of permethyldecasilane [**1**, $Me(SiMe_2)_{10}Me$] with γ-cyclodextrin (γ-CD), indicating that the silicon main chain of **1** penetrating three γ-CD rings per a decasilane adopts an all-trans rod-like conformation in water.

When a heterogeneous mixture of a powder of **1** (9.0×10^{-5} mol)[10] and γ-CD (8.9×10^{-4} mol) in water (5.0 mL) was stirred at room temperature for 2 days, a homogeneous suspension formed. The solid particles were collected by filtration and washed with water and then THF to remove excess γ-CD and free **1**. Drying the residual under vacuum gave a complex of **1** with γ-CD (**1**/γ-CD) as a white powder in 55% yield.[11] The mol ratio of γ-CD to **1** in the inclusion complex was determined by a ^{1}H NMR spectrum in a pyridine-d_5 solution. On the basis of the intensity ratio of the peaks at 5.71 ppm (C1-protons of γ-CD) to those at 0.14–0.33 ppm (methyl protons of permethyldecasilane), one molecule of **1** penetrated three γ-CD molecules.[12] The result is in good accordance with that obtained by Harada et al.[9] They have shown that three silylene units corresponds to the cavity depth of a γ-CD molecule by analyzing the ^{1}H NMR spectra of permethylpolysilane/γ-CD inclusion complexes. No complex formation of **1** with α- and β-cyclodextrins were observed. As shown in Figure 1, the cavity size of γ-CD (the narrower caliber, 8.5 Å) is large enough to be penetrated by **1** with an all-trans rod structure (a rough diameter of a section of the rod, ca. 6 Å), while the sizes of the α- and β-CD cavities are too small for **1** to penetrate the cavities.



γ-Cyclodextrin (γ-CD) Permethyldecasilane 1

Figure 1. Structures of γ-CD and permethyldecasilane (**1**).

The formation of complex **1**/γ-CD was evidenced by a solid-state CP-MAS ^{13}C NMR study. While the ^{13}C resonances of C1 and C4 of γ-CD appear usually as multiplets because of the partly distorted glucose rings of an uncomplexed γ-CD (Figure 2a), the corresponding resonances of the inclusion complex were observed as two singlets (Figure 2b), showing that all the glucose rings of γ-CD are equivalent in the complex. These results support that γ-CD molecules form a channel-type complex with **1**. Similar spectral changes have been observed for various inclusion complexes of CDs with linear polymers such as poly (dimethylsiloxane).[13]

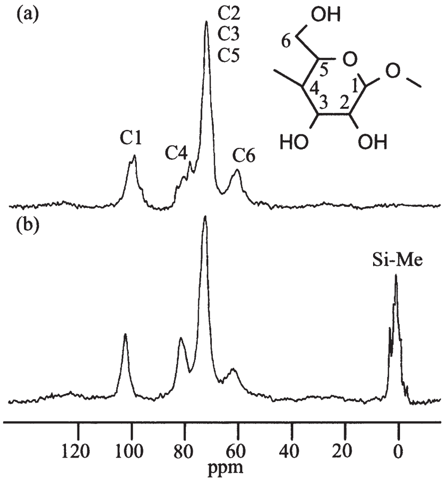


Figure 2. CP-MAS ^{13}C NMR spectra of (a) γ-CD and (b) **1**/γ-CD.

Decasilane **1** was insoluble but **1**/γ-CD was slightly soluble in water (up to ca. 10^{-6} M), and hence, UV absorption and fluorescence spectra of the complex in water were successfully

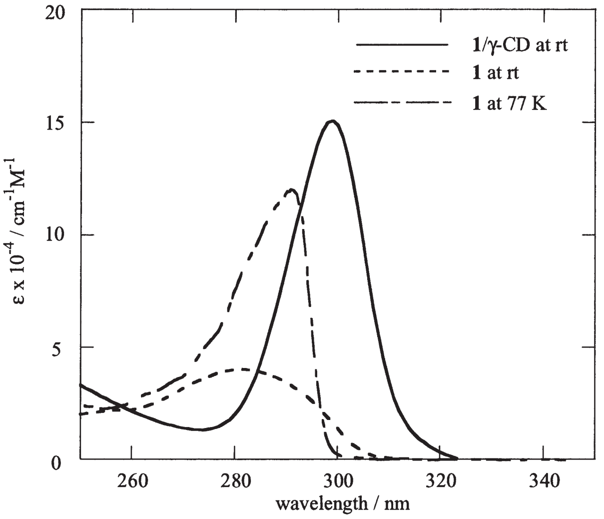


Figure 3. Absorption spectra of **1** in 3-methylpentane at room temp (broken line) and 77 K (dash-dotted line) and that of **1**/γ-CD in water at room temp (solid line).

recorded. In a previous paper, we have shown that the UV spectrum of **1** is remarkably temperature dependent in 3-methylpentane;[5b] as shown in Figure 3, a broad absorption band at 282 nm at room temperature red-shifts to 294 nm with a narrower bandwidth at 77 K. The absorption spectrum of **1**/γ-CD in water at room temperature was remarkably different from those of **1** in 3-methylpentane; the absorption maximum for **1**/γ-CD (299 nm) red-shifted 17 nm and 5 nm from those for **1** at room temperature and 77 K, respectively, and the bandwidth for **1**/γ-CD was comparable with that for **1** at 77 K. The characteristic spectral feature of **1**/γ-CD in water is indicative that the decasilane main-chain should have an all-trans zig-zag conformation in γ-CD cavities, as schematically shown in Figure 4. The 5 nm difference of the absorption maxima between **1** at 77 K and **1**/γ-CD at room temp indicates a slight difference in the main-chain conformation of **1** between the two environments; the main-chain conformaition of **1** in γ-CD is suggested to be closer to an ideal all-trans zig-zag conformation than a loose helical psuedo all-trans conformation (transoid conformation)[14] of **1** in low-temperature solutions.

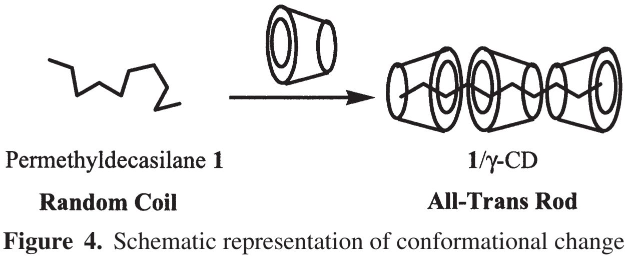


Figure 4. Schematic representation of conformational change of **1** induced by complexation with γ-CD.

A fluorescence band maximum of **1**/γ-CD in water was observed at 318 nm, which is a little red-shifted from that of **1** in 3-methylpentane at room temperature (Figure 5).[4,5] In contrast to the excitation spectra of **1** in 3-methylpentane showing very low emission efficiency at the higher excitation frequences, an excitation spectrum of **1**/γ-CD monitored at 299 nm was in good accordance with the absorption spectrum, indicating the rigid all-trans rod-like main-chain of **1** in the inculsion complex.

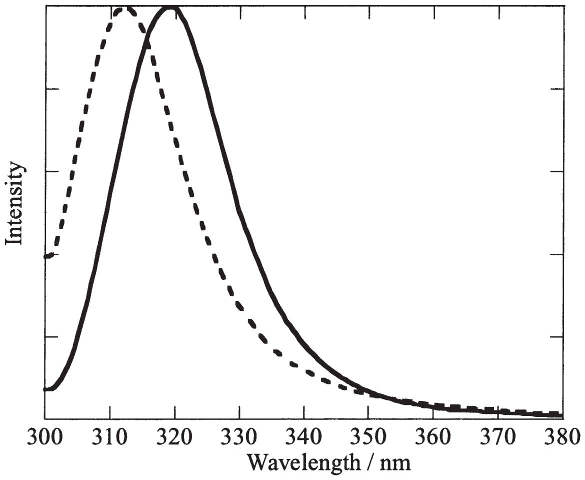


Figure 5. Fluorescence spectra of **1** in 3-methylpentane (broken line) and **1**/γ-CD in water (solid line) at room temp.

References and Notes

1 For reviews of polysilanes, see: R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989); R. West, in "The Chemistry of Organic Silicon Compounds, Part 1," ed. by S. Patai and Z. Rappoport, John Wiley & Sons, Chichester (1989), Chap. 19, p 1207.

2 L. A. Harrah and J. Zeigler, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 309 (1985); P. Trafenos, III, J. R. Damewood, Jr., R. West, and R. D. Miller, *Organometallics*, **4**, 1318 (1985).

3 H. S. Plitt and J. Michl, *Chem. Phys. Lett.*, **198**, 400 (1992); H. S. Plitt, J. W. Downing, M. K. Raymond, V. Balaji, and J. Michl, *J. Chem. Soc., Faraday Trans.*, **90**, 1653 (1994).

4 a) K. Obata, C. Kabuto, and M. Kira, *J. Am. Chem. Soc.*, **119**, 19345 (1997). b) K. Obata and M. Kira, *Chem. Commun.*, **1998**, 1309. c) K. Obata and M. Kira, *Organometallics*, **18**, 2216 (1999).

5 For a review on photochemistry of organosilicon compounds, see: M. Kira and T. Miyazawa, in "The Chemistry of Organic Silicon Compounds, Vol. 2," ed. by Z. Rappoport and Y. Apeloig, John Wiley & Sons, Chichester (1998), Chap. 22, p 1311.

6 a) S. Mazières, M. K. Raymond, P. A. Raabe, and J. Michl, *J. Am. Chem. Soc.*, **119**, 6682 (1997). b) I. Roman, H. Teramae, and J. Michl, *Chem. Phys. Lett.*, **270**, 500 (1997).

7 K. Tamao, H. Tsuji, M. Terada, M. Asahara, S. Yamaguchi, and A. Toshimitsu, *Angew. Chem., Int. Ed.*, **39**, 3287 (2000).

8 For a recent review on inclusion complexes of cyclodextrins, see: A. Harada, *Acc. Chem. Res.*, **34**, 456 (2001).

9 H. Okumura, Y. Kawaguchi, and A. Harada, *Macromol. Rapid Commun.*, **23**, 781 (2002).

10 T. Yatabe, A. Kaito, and Y. Tanabe, *Chem. Lett.*, **1997**, 799.

11 **1**/γ-CD: a white powder; mp 280 °C (decomp.); ^{13}C CP-MAS NMR (75 MHz) δ -2.4 (br, Si-Me), 60.6 (br), 72.7 (br), 81.8 (br), 104.1 (br). ^{29}Si CP-MAS (59 MHz) δ −40.8, −37.1, −34.6, −13.5 (one peak was overlapped).

12 It was not determined by the NMR spectrum whether the complex **1**/γ-CD dissociated in pyridine-d_5.

13 H. Okumura, M. Okada, Y. Kawaguchi, and A. Harada, *Macromolecules*, **33**, 4297 (2000); H. Okumura, Y. Kawaguchi, and A. Harada, *Macromolecules*, **34**, 6338 (2000).

14 J. Michl and R. West, *Acc. Chem. Res.*, **33**, 821 (2000).