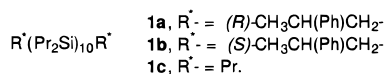# Induction of Helical Chirality in Linear Oligosilanes by Terminal Chiral Substituents

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Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN) 19-1399 Koeji, Nagamachi Aoba-ku, Sendai 980, Japan Department of Chemistry, Graduate School of Science Tohoku University Aoba-ku, Sendai, 980-77, Japan

Thermochromic behavior of linear peralkylpolysilanes and long-chain oligosilanes exhibited in solution and in the solid state has been studied extensively, and the origin is usually ascribed to a random coil-to-rod transition of the silicon backbone.[1−3] The rigid rod-like structures favored at low temperatures are often described as *all-trans* planar conformations of the silicon backbone with the dihedral angles (θ) of 180° for all the Si tetrads, but in reality, loose-helical conformations with the θ values of 165−170° (15/7 helix) should be adopted, as many theoretical calculations for peralkyloligosilanes and polysilanes have suggested.[4] It is an interesting issue whether the helical chirality of a polysilane backbone is regulated by the chirality of the terminal chiral groups. We report herein synthesis and structure of novel linear eicosapropyldecasilanes with two chiral aralkyl substituents at the terminal silicon atoms **1a** and **1b**.[5,6] Remarkably, these oligo-

$$R^*(Pr_2Si)_{10}R^* \qquad \begin{array}{l} \textbf{1a, } R^* = (R)\text{-}CH_3CH(Ph)CH_2\text{-} \\ \textbf{1b, } R^* = (S)\text{-}CH_3CH(Ph)CH_2\text{-} \\ \textbf{1c, } R^* = Pr\text{-} \end{array}$$

silanes show sharp and intense circular dichroism (CD) spectra at low temperatures due to the helical chirality of the silicon chain. While interesting helical polysilane polymers with chiral alkyl substituents have been prepared,[7] the origin of the helicity has not been discussed in detail.

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(1) For reviews of polysilane polymers, see: (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989,** *89,* 1359. (b) Zeigler, J. M. *Synth. Met.* **1989,** *28,* C581. (c) West, R. *J. Organomet. Chem.* **1986,** *300,* 327. (d) West, R. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons: Chichester, 1989; Chapter 19, p 1207.
(2) (a) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985,** *23,* 209. (b) Trefonas, P., III; Damewood, J. R., Jr.; West, R.; Miller, R. D. *Organometallics* **1985,** *4,* 1318.
(3) For other explanations of the thermochromism, see: Shukla, P.; Cotts, P. M.; Miller, R. D.; Russell, T. P.; Smith, B. A.; Wallraff, G. M.; Baier, M.; Thiyagarajan, P. *Macromolecules* **1991,** *24,* 5606.
(4) (a) Welsh, W. J.; Johnson, W. D. *Macromolecules* **1990,** *23,* 1881. (b) Patnaik, S. S.; Farmer, B. L. *Polymer* **1992,** *33,* 5121. (c) Plitt, H. S.; Michl, J. *Chem. Phys. Lett.* **1992,** *198,* 400. (d) Plitt, H. S.; Downing, J. W.; Raymond, M. K.; Balaji, V.; Michl, J. *J. Chem. Soc., Faraday Trans.* **1994,** *90,* 1653. (e) Sun, H. *Macromolecules* **1995,** *28,* 701. (f) Albinsson, B.; Teramae, H.; Downing, J. W.; Michl, J. *Chem. Eur. J.* **1996,** *2,* 529. (g) Imhof, R.; Teramae, H.; Michl, J. *Chem. Phys. Lett.* **1997,** *270,* 500.
(5) Because the mixture of **1a/1b** was not separated by any of the chiral HPLC columns we tried, the enantiomeric excess (ee) values were estimated to be 97 and 98%, respectively, on the basis of the ee values of (*R*)- and (*S*)-2-phenylpropyl alcohols from which **1a** and **1b** were derived; the ee values of the alcohols were determined using chiral HPLC columns (DAICEL CHIRALCEL-OB). The experimental details are given in the Supporting Information.
(6) Preparation procedures and spectral data of **1a−c** and related compounds are shown in the Supporting Information.
(7) (a) Matyjaszewski, K. *J. Inorg. Organomet. Chem.* **1992,** *2,* 5. (b) Frey, H.; Möller, M.; Matyjaszewski, K. *Macromolecules* **1994,** *27,* 1814. (c) Frey, H.; Möller, M.; Turetskii, A.; Lotz, B.; Matyjaszewski, K. *Macromolecules* **1995,** *28,* 5498. (d) Fujiki, M. *J. Am. Chem. Soc.* **1994,** *116,* 6017. (e) Fujiki, M. *J. Am. Chem. Soc.* **1994,** *116,* 11976. (f) Fujiki, M. *Appl. Phys. Lett.* **1994,** *65,* 3251.
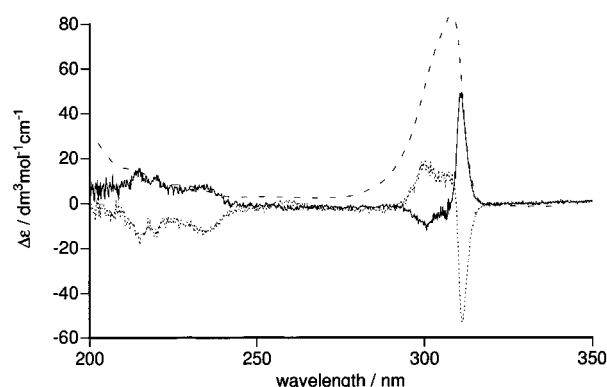

Figure 1. UV−vis (− − −) and CD spectra (−) of **1a** (5.68×10^{-5} M) and CD spectrum of **1b** (5.79×10^{-5} M) (- - -) in isopentane/methylcyclohexane (5/1) matrices at 85 K. The absorbance of the UV−vis spectrum of **1a** is shown in an arbitrary unit.

Since the UV−vis spectral features of **1a**, **1b**, and **1c** are identical to each other, terminal chiral 2-phenylpropyl groups are not taken to affect the electronic properties or the conformational preference of the silicon backbone. As shown in Figure 1, **1a** with (*R*)-2-phenylpropyl substituent shows a sharp and strong positive Cotton band at 315 nm at 85 K in the CD spectrum. The oligosilane **1b** with (*S*)-2-phenylpropyl substituent shows a similar but negative Cotton band at the same temperature. Both the CD spectra are strongly temperature dependent; the Cotton bands disappear at higher temperatures than 153 K. The results indicate that the terminal chiral groups induce the helical chirality of the silicon backbone at low temperatures. It is interesting to note that the CD bands are much sharper than the corresponding absorption bands at the same temperature; the CD band of **1a** overlaps only at the lower energy end of the absorption band as shown in Figure 1. The helical coil conformer would not be the most prominent conformer of the decasilane even at 85 K. The comparison between the absorption and CD spectra also indicates that there is no population of the *all-trans* conformer in the rigorous sense ($\theta = 180°$), which is expected to show lower energy absorption than the loose-helix conformer due to the more effective σ conjugation in the former.[8]

While a number of theoretical calculations of permethyloligosilanes and polysilanes have revealed that the most stable structure is an approximately 15/7 helix ($\theta = 172°$) due to the steric interaction between methyl groups at 1,3-silicon atoms,[4] there has been no detailed molecular mechanics study of the peralkyloligosilanes with longer alkyl groups than methyl reported.[9] The MM2 force-field calculations were performed for tetradecapropylhexasilane (**2c**).[10] Among a number of possible propyl side-chain arrangements, one *trans* (T, CSiCC dihedral angle (α) = 180°) and two *gauche* (G and G′, α = 60° and −60°, respectively) conformations are considered in input structures. Notably, conformer TtTt with *all-trans* propyl groups is 20 kcal/mol higher in energy than the lowest energy conformer GtTg1, which has a loose-helix structure of the silicon backbone with the positive θ value of 172° (Figure 2);[11] repulsion between propyl groups at vicinal two silicon atoms in TtTt structure is avoided effectively in GtTg structures. The MM2 calculations suggest that the conformers responsible for

(8) The origin of a weak and broad band at around 300 nm with the opposite sign of the main peak in the CD spectrum of each enantiomer is unclear at this moment. See refs 4f and 4g for the more complicated features of the conformational effects in UV spectra of oligosilanes.
(9) MM2 calculations of 1,5-dimethyl(deca-*n*-hexyl)pentasilane have been performed: Damewood, J. R., Jr. *Macromolecules* **1985,** *18,* 1793.
(10) Standard parameters for organosilicon compounds proposed by Allinger et al. were used for the present calculations: Frierson, M. R.; Imam, M. R.; Zalkow, V. B.; Allinger, N. L. *J. Org. Chem.* **1988,** *53,* 5248.
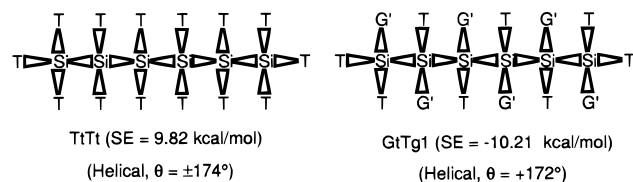
Figure 2. Schematic representation of conformers TtTt and GtTg1 of **2c** with *all-trans*-like silicon backbone.[11] Their steric energies (SE), the helical properties, and the dihedral angles of Si tetrads are shown in parentheses.

the CD bands of **1a** and **1b** will have GtTg1-type repetition of propyl side chains and that **1a** prefers the right-handed helix, while **1b** the left-handed helix.

The X-ray crystallographic analysis of a single crystal of 1,6-bis[(*R*)-2-phenylpropyl]dodecapropylhexasilane (**2a**)[12,13] has shown that the silicon backbone is loose-helical with the negative helicity ($\theta = -172°$ to $177°$) (Figure 3), where the arrangement of the propyl side chains as well as the helicity is different from those found by MM2 calculations. At the most

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(11) The conformers are specified by symbols like GgTt, which means that a silicon atom with two *gauche* propyl groups is neighbored by a silicon atom with two *trans* propyl groups; upper and lower propyl groups concerning the silicon backbone in Figure 2 are indicated by uppercase and lowercase characters, respectively. Several other GtTg conformers as well as various GgGg and GgTt conformers are also much less stable than conformer GtTg1 shown in Figure 2. Conformer GtTg1 is ca. 4 kcal/mol more stable than any conformer with one gauche Si tetrad; the energy difference is much larger than that for permethyldecasilane (0.43 kcal/mol).

(12) Permethyldodecasilane has recently been shown by the X-ray analysis to have an almost *all-trans* silicon backbone in a film prepared by a CVD method: Yatabe, T.; Shimomura, M.; Kaito, A. *Chem. Lett.* **1996**, 551.

(13) Crystal data of **2a**: MF = $C_{54}H_{106}Si_6$, MW = 923.94, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 9.74(3)$, $b = 67.6(3)$, and $c = 9.292(4)$ Å, $V = 6118(23)$ Å^3, $Z = 4$, $D_{calcd} = 1.003$ g cm^{-3}, $F(000) = 2056.00$, $\mu = 14.87$ cm^{-1}. Data collection (170 K): a Rigaku AFC5R diffractometer, graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å), a rotating anode generator (45 kV, 200 mA), ω scan mode, scan speed of 8.0°/min (in ω), $2\theta_{max} = 128.2°$. A total of 5651 reflections were measured (twice of independent reflections), of which 4725 reflections [$I > 3.0\sigma(I)$] were used in the refinement. The final R value = 0.075 ($R_w = 0.101$), GOF = 3.29, $\rho_{max} = 0.38$, $\rho_{min} = -0.32$ eÅ^{-3}.
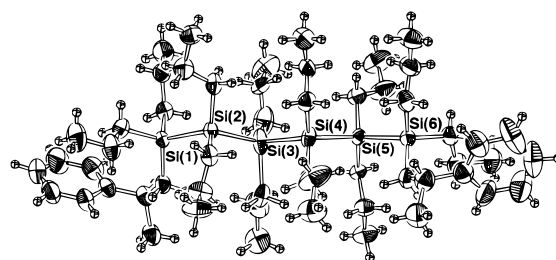

Figure 3. X-ray structure of **2a** (ORTEP plot), showing the atom-numbering scheme. Selected bond distances (Å): Si(1)−Si(2) 2.364, Si(2)−Si(3) 2.361, Si(3)−Si(4) 2.347, Si(5)−Si(6) 2.376. Selected bond angles (deg): Si(1)−Si(2)−Si(3) 110.20, Si(2)−Si(3)−Si(4) 111.38, Si(3)−Si(4)−Si(5) 111.19, Si(4)−Si(5)−Si(6) 110.01. Selected dihedral angles (deg): Si(1)−Si(2)−Si(3)−Si(4) −175.70, Si(2)−Si(3)−Si(4)−Si(5) −167.80, Si(3)−Si(4)−Si(5)−Si(6) −174.30.

stable MM2 structure, **2a** has the GtTg repetition of the propyl side chains with the two chiral groups on the long axis similarly to perpropylhexasilane. On the other hand, in the single crystal of **2a**, two R* groups occupy the side-chain positions and the two T and two G propyls are faced at the central SiSi bond. The MM2 energy of the latter structure is ca. 4 kcal/mol higher than that of the MM2 structure, suggesting that the crystal packing force will be larger than the intrinsic conformational energy difference.