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σ-Conjugation in a Periodic Polycarbosilane, Poly[1,1,2,2-tetramethyldisilylenemethylene]

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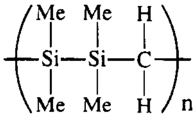
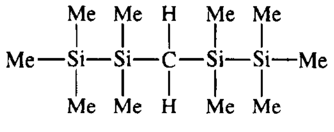
Polysilylene[1] and polyethylene have *homocatenated* skeletons composed of silicon and carbon atoms, respectively. It has been shown experimentally that the skeleton absorption energies due to $\sigma-\sigma^*$ transitions in both the silicon and carbon catenates become lower as the number of atoms in the catenates increases; poly(dimethylsilylene) (PDMS) shows absorption at around 4.28 eV (290 nm) while hexamethyldisilane absorbs around 6.53 eV (190 nm), polyethylene absorbs near 8.27 eV (150 nm), and ethane absorbs near 9.19 eV (135 nm).[2] These bathochromic shifts are qualitatively explained by σ-conjugation, which is the interaction between σ-orbitals along the chain axis.[3,4] These σ-orbital interactions depend on the helical conformation: as the helical angle of the polysilylene decreases, the σ-orbital interaction becomes smaller, following the blue shift of absorption.[4] For example, the lowest absorption peak energy of poly(dihexylsilylene) (PDHS) is observed to shift from 3.33 eV (372 nm) to 3.92 eV (316 nm) as a result of a conformational transition.[5] σ-Conjugation in the *homocatenates* has also been investigated theoretically. One of the authors (H.T.) and his co-worker have calculated the following effective hole masses at the top of the valence bands of trans-planar polysilylene and trans-planar polyethylene: $0.13m_0$ for polysilylene and $0.21m_0$ for polyethylene, where m_0 is the mass of a free electron.[4] These results indicate that σ-electrons are delocalized in *homocatenates* such as −SiSiSi− and −CCC− because the effective hole masses of these polymers are smaller than that of a free electron. The question still remains, however, both experimentally and theoretically, as to whether σ-electrons delocalize in *heterocatenates* such as −SiSiC−.

To clarify this, we prepared a periodic polycarbosilane,[6] poly[1,1,2,2-tetramethyldisilylenemethylene] (**1**), and compared its absorption spectrum to those of two model compounds **2** and **3**.[7] The observed bathochromic shifts for **1** and **2** relative to **3** indicate the effect of σ-conjugation along the skeleton. This is further supported by the small value of the calculated effective hole mass in the trans-planar parent polycarbosilane, poly(disilylenemethylene) (**4**).



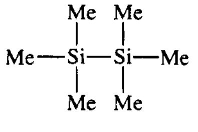
$$\left(-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\right)_n$$

1



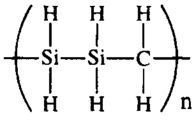
$$\mathrm{Me}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{Me}$$

2



$$\mathrm{Me}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{Me}$$

3



$$\left(-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{Si}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{Si}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\right)_n$$

4

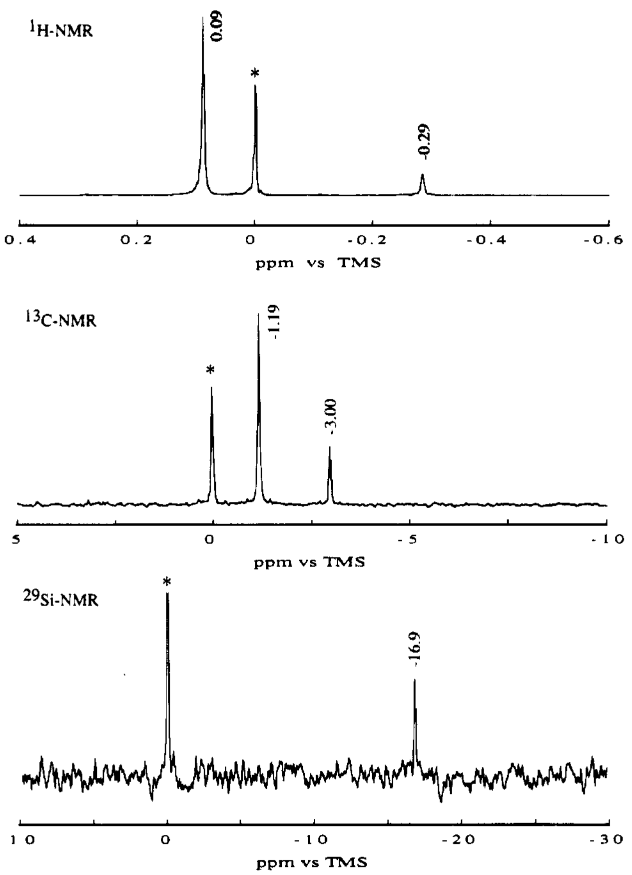


Figure 1. ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra of **1** in $CDCl_3$ at 20 °C. Asterisks indicate the tetramethylsilane internal signals.

Polycarbosilane **1** was synthesized by Wurtz coupling with crown ether.[8] A total of 5.0 g (25 mmol) of bis(chlorodimethylsilyl)methane[9] was added dropwise to 50 mL of toluene including 1.4 g (61 mmol) of dispersed sodium and 0.6 g (2.7 mmol) of 15-crown-5. After 8 h of reflux, the reaction mixture was filtered, and the filtrate was poured dropwise into the excess ethanol. The resulting polymer was purified twice by reprecipitation from toluene solution with ethanol, giving 138 mg of **1** (yield: 4.1%). The molecular weight of **1**, obtained by GPC measurement based on polystyrene standards, was $M_n = 1.3 \times 10^5$ ($M_w/M_n = 4.6$).

Figure 1 shows the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra of **1**.[10] In the ^{1}H-NMR spectrum, there are two singlet resonance peaks, one at 0.09 ppm for the methyl protons of the substituents and one at −0.29 ppm for the methylene protons of the skeleton. In the ^{13}C-NMR spectrum, the two singlet resonance peaks appear at −1.19 (methyl carbon) and −3.00 ppm (methylene carbon). The ^{29}Si-NMR spectrum shows one singlet peak at −16.9 ppm for the disilylene unit of the skeleton. The ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra are consistent with those for **1** in the periodic catenated structure of SiSiC sequences. These NMR spectra and GPC measurements confirm the absence of small cyclic oligomers in **1**.

Figure 2 shows the UV absorption spectra of **1** (solid line), **2** (dotted line), and **3** (broken line) in isooctane solutions at room temperature.[11] All observed absorption bands are assigned to $\sigma-\sigma^*$ excitation of the skeletons. As the number of disilylene units increases, the $\sigma-\sigma^*$ transition energy (E_{max}) in the SiSiC heterocatenate becomes lower: **3**, 6.45 eV (192.1 nm); **2**, 6.40

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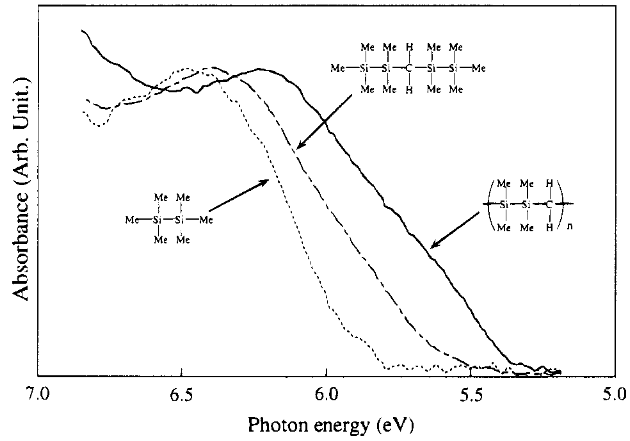

Figure 2. Absorption spectra of **1** (solid line), **2** (dotted line), and **3** (broken line) in isooctane solutions at 25 °C. All spectra are normalized by the lowest absorption peaks.

eV (193.8 nm); and **1**, 6.21 eV (199.6 nm). Furthermore, the spectral profiles of **1** and **2** have tails toward the lower energy regions. If there was no interaction between neighboring disilylene units, the $\sigma-\sigma^*$ transition energy and absorption profiles should be the same for all three compounds. Thus, the observed bathochromic shift must result from σ-conjugation between the disilylene units via the methylene units. Although **2** can be regarded as an analog of pentane and pentasilane, the degree of observed energy shift (ΔE_{obs}) between $E_{\max}$ of the polymers and the oligomers varies with the types of catenation.[2] In the present SiSiC heterocatenate, ΔE_{obs} between **1** and **2** is calculated to be 0.19 eV. In the CCC homocatenate, although the $E_{\max}$ of pentane is not reported, ΔE_{obs} between polyethylene and butane (8.55 eV; 145 nm) is only 0.28 eV. In the case of pentane, ΔE_{obs} is expected to be even smaller. In contrast, in the SiSiSi homocatenate, ΔE_{obs} between PDMS and permethylpentasilane (4.96 eV; 250 nm) is 0.78 eV, far larger than that for the other types of catenation. Recently, Tachibaba *et al.* assigned the lowest absorption bands of polysilylenes to an excitonic transition state, and not to the interband transitions.[12] The exciton state is induced by Coulombic interaction within a photoexcited electron–hole pair, and the excitonic transition energy is generally lower than the interband transition energies. Actually, the estimated $\sigma-\sigma^*$ interband transition energy of PDHS obtained by electroabsorption and two-photon absorption spectroscopy is 4.6 eV (270 nm), which is higher than the observed lowest excitonic absorption energy (3.4 eV; 365 nm). Thus, the large ΔE_{obs} in the SiSiSi homocatenate is attributed to the exciton effect. It is not clear, at present, whether the observed absorption band of **1** is due to an interband transition or an excitonic transition. Nevertheless, the observed bathochromic shift qualitatively indicates, at least, the effect of σ-conjugation in the SiSiC heterocatenate.

For theoretical confirmation of this, we calculated the effective hole masses (m_h^*) at the top of the valence-band edges and the ionization potentials (IP) of polyethylene, polysilylene, and **4**.[13] Table 1 lists the m_h^* and IP of these polymers taken from the calculated energy-band structure by an *ab initio* crystal orbital method with a 3-21G basis set. In this calculation, we assumed that the geometrical structures are in a trans-planar conformation to avoid conformation problems. The other geometrical parameters of **4** were fully optimized by the energy gradient method.[14] Those of polyethylene and polysilylene were taken from a previous report.[4,15] The m_h^* of **4** ($0.18m_0$) is as small as that of the other polymers, and this small m_h^* value indicates that a σ-electron can delocalize in the *heterocatenate* with –SiSiC–. In addition, the IP and m_h^* of **4** are comparable to those of polysilylene, which suggests that conductivity in the polycarbosilane can be increased by choosing the appropriate dopants, as with polysilylenes.[1,4]

Table 1. Effective Hole Masses at the Valence-Band Edge and Koopmans' Ionization Potentials of Polyethylene, the Parent Polysilylene, and the Parent Polycarbosilane, Poly(disilylenemethylene) (All Calculations Are at the 3-21G Level)[a]

compound[b]	eff. mass, m_0[c]	IP, eV
polyethylene (–CCC–)	0.20	10.54
polysilylene (–SiSiSi–)	0.13	8.92
poly(disilylenemethylene) (–SiSiC–)	0.18	9.00

[a] The geometries of the polymers are in the trans–planar conformation. [b] The catenated sequences of the polymers are in parentheses. [c] Units are free-electron mass.

Our experimental and theoretical results have revealed σ-conjugation in the periodic polycarbosilane having –SiSiC– catenates. The spectral similarity between **1** and **3** suggests that the $E_{\max}$ of the periodic polycarbosilane is controllable by changing the periodic sequence, $-(\text{Si}_m\text{C})_n-$ (m = 1, 2, 3, ...). Consequently, periodic polycarbosilanes are applicable to optoelectronic materials because of the 6.0-eV optical bandgap and the small effective hole mass. We are now continuing studies on **1** and its related compounds, as well as other periodic polycarbosilanes, for a more quantitative analysis.

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References and Notes

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(7) (1) Compound **2**, 2,2,3,3,5,5,6,6-octamethyl-2,3,5,6-tetrasilaheptane, was prepared by Grignard coupling of pentamethylchlorodisilane and dibromomethane in THF solution at room temperature. ^{1}H-NMR (CDCl_3): 0.09 (12H, SiMe_2), 0.04 (18H, SiMe_3), –0.26 ppm (2H, CH_2). ^{13}C-NMR (CDCl_3): –1.25 (SiMe_2), –2.38 (SiMe_3), –2.77 ppm (CH_2). ^{29}Si-NMR (CDCl_3): –17.2 (SiMe_2), –19.6 ppm (SiMe_3). MS (EI, 70 eV) *m/e* (relative intensity): 276 (M^+, 9), 261 (3), 203 (100), 187 (46), 173 (12), 145 (38), 129 (54), 115 (19), 73 (94). (2) Compound **3**, hexamethyldisilane, was purchased from Shin-Etsu Chemical and was used without further purification.

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(9) (a) Bis(chlorodimethylsilyl)methane was prepared from bis(trimethylsilyl)methane according to the reported procedure.

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(10) ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{29}Si (60 MHz) NMR spectra were recorded with a Varian Unity-300 FT-NMR spectrometer. The sample was dissolved in $CDCl_3$. Tetramethylsilane was used as the internal standard.

(11) Absorption spectra were recorded with a JASCO VUV-500 vacuum UV spectrophotometer.

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(13) For details of the calculation method, see ref 4.

(14) The optimized structure of **4** is as follows: $r_{\mathrm{Si-Si}} = 2.391$ Å, $r_{\mathrm{Si-C}} = 1.922$ Å, $\angle$Si–Si–C = 111.3°, $\angle$Si–C–Si = 115.6°, $r_{\mathrm{Si-H}} = 1.492$ Å, $r_{\mathrm{C-H}} = 1.088$ Å, $\angle$H–Si–H = 107.2°, $\angle$H–C–H = 106.9°.

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