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Synthesis and Optical Properties of the Si_4C-Type Periodic Polycarbosilane Poly[(octamethyltetrasilylene)methylene]

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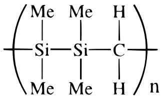
ABSTRACT: Poly[(octamethyltetrasilylene)methylene] was prepared by the Wurtz reaction of bis(chlorotetramethyldisilanyl)methane. The periodic structure with Si_4C-type sequences was characterized by ^{1}H-, ^{13}C-, and ^{29}Si-NMR. An investigation of the UV absorption and photoluminescence properties of this polymer in solid-state film revealed the unique character of Si_4C-type periodic polycarbosilane. The $\sigma-\sigma^*$ transition energy varied from 5.2 to 4.5 eV due to conformation. The strong Stokes shift (1.2 eV) indicated that the emission is due to a "self-trapped" exciton state, in which excitation is weakly delocalized in a skeleton with a nonvertical geometry.

I. Introduction

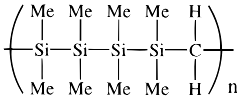
Inorganic polymers based on saturated linear skeletons of group 14 atoms such as polysilanes and polygermanes have received much attention during the past decade as model compounds for one-dimensional materials. These polymers have characteristic electronic structures in which σ-electrons are delocalized along the polymer chains.[1,2] Moreover, it has been possible to vary the fundamental absorption ($E_{\max}$) of polysilanes and polygermanes in a range between 3 and 4 eV by controlling polymer conformation[3,4] and introducing functional substituents.[5,6] These σ-conjugated electronic structures contribute to their potential applications in various areas including as photoresists in microlithography, photoconductive polymers,[7−11] polymeric semiconducting materials,[12−14] nonlinear optics,[15−17] and organic electroluminescence devices.[18−20] Furthermore, experimental and theoretical studies have indicated that σ-conjugated polymers with heterostructures are of great scientific interest; the interfaces between different band-gap phases in polysilane films are regarded as one-dimensional heterojunctions,[21] and periodic polymers consisting of silicon and other elements correspond to a one-dimensional superlattice.[22] We have reported two types of periodic polymer with Si_2Ge sequences[23] and Si_2C sequences.[24] However, the $E_{\max}$ of the Si_2Ge-type periodic polymer is similar to those of homopolymers because of the small energy difference between silicon and germanium atoms.[25,26] In terms of modulating σ-conjugated electronic structures, a combination of silicon and carbon atoms is more promising. Actually, the $E_{\max}$ of Si_2C-type periodic polycarbosilane poly[(tetramethyldisilylene)methylene] (**1**) has been observed near 6.2 eV (200 nm), and this $E_{\max}$ value drastically shifted both from those of poly(dimethylsilylene) (6.64 eV, 340 nm) and polyethylene (8.27 eV, 150 nm).[27−29] An *ab initio* calculation indicated that the σ-electron in Si_2C heterocatenate is delocalized in spite of the large energy difference between silicon and carbon atoms. In addition, the similarity in the $E_{\max}$ values of **1** and hexamethyldisilane (Me_6Si_2) suggests that their electronic structures can be controlled by changing their periodic sequences.

In order to probe their potentiality as heterostructured σ-conjugated polymers, we have investigated various types of periodic polycarbosilanes and their model compounds. This paper describes the synthesis and optical properties of an Si_4C-type periodic polycarbosilane, poly[(octamethyltetrasilylene)methylene] (**2**). Our results indicate that periodic polycarbosilanes are a new class of σ-conjugated polymer and that their electronic structures are different from those of ordinary polysilanes.



$\left(\mathrm{SiMe_2{-}SiMe_2{-}CH_2}\right)_n$

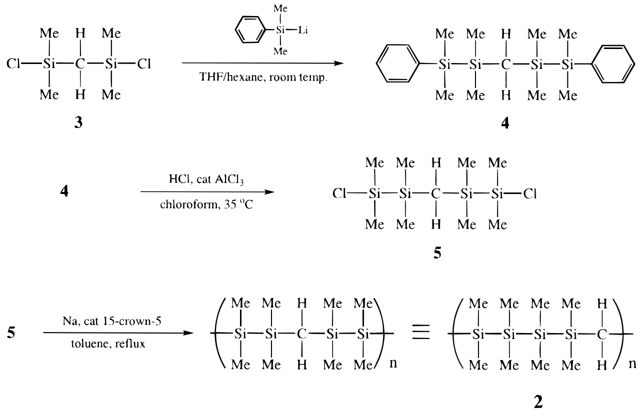
1



$\left(\mathrm{SiMe_2{-}SiMe_2{-}SiMe_2{-}SiMe_2{-}CH_2}\right)_n$

2

Scheme 1



II. Results and Discussion

Synthesis and Characterization. Polymer **2** was synthesized in a three-step reaction as summarized in Scheme 1. (Dimethylphenylsilyl)lithium ($Me_2PhSiLi$) in THF solution was added to a solution of bis(chlorodimethylsilyl)methane (**3**) in hexane at room temperature, giving bis(1-phenyltetramethyldisilanyl)methane (**4**) in 39.4% yield. Chlorodephenylation of **4** in chloroform with HCl and $AlCl_3$ gave bis(1-chlorotetramethyldisilanyl)methane (**5**) in 62.5% yield. Both **4** and **5** were characterized by ^{1}H-, ^{13}C-, and ^{29}Si-NMR, mass spectroscopy, and elemental analysis. The analytical data are described in the Experimental Section.

The polymerization was done by dropwise addition of **5** into dispersed sodium and 15-crown-5 in refluxed toluene. It was noted that polymerization did not

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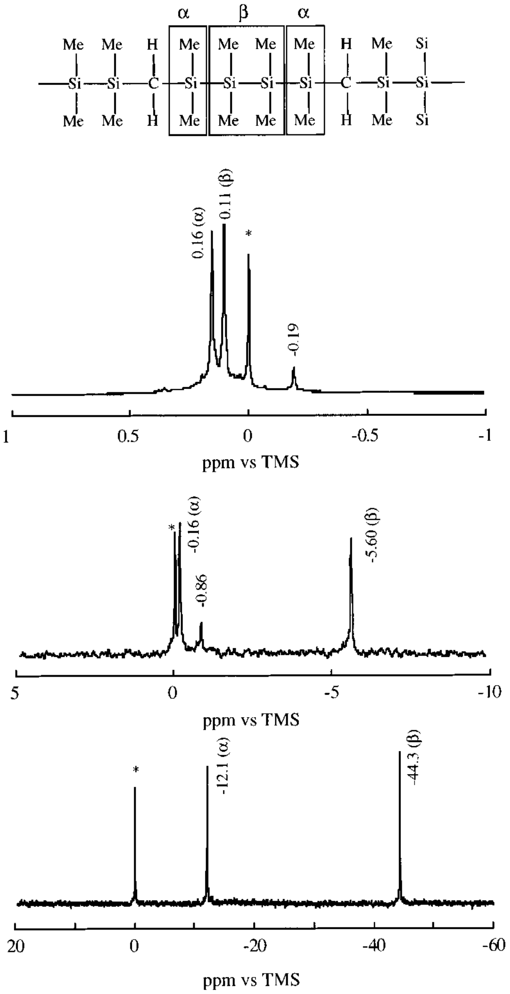

Figure 1. ^{1}H-, ^{13}C-, ^{29}Si-NMR spectra of **2** in $CDCl_3$ at 25 °C. Asterisks indicate the signals of tetramethylsilane internal standard.

proceed without crown ether.[30] The resulting polymer was purified twice by reprecipitation from the toluene solution with methanol, giving 250 mg of **2** as a white waxy solid in 7.3% yield. The overall yield based on **3** was 1.8%. The molecular weight of **2**, obtained by GPC measurement based on polystyrene standards, was $M_n = 2.7 \times 10^3$ ($M_w/M_n = 1.19$). The DSC measurement gave two transition points at 205 (T_g) and 310 K (T_m).

Figure 1 shows the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra of **2**. The ^{1}H-NMR spectrum shows two resonance peaks for methyl protons: 0.16 ppm at the α position of the tetrasilylene units, and 0.11 ppm at the β position, where the α position indicates dimethylsilylenes adjacent to methylene units, and the β position indicates the others. The resonance peak for methylene protons appears at −0.19 ppm. In the ^{13}C-NMR spectrum, the one singlet resonance peak for methylene carbon appears at −0.86 ppm, and the two singlet peaks for methyl carbon at the α and β positions appear at −0.16 and −5.60 ppm, respectively. The ^{29}Si-NMR spectrum shows two singlet peaks at −12.1 ppm for the α silicon and the other at −44.3 ppm for the β silicon of the tetrasilylene units. These NMR spectra revealed that **2** consisted of a periodic catenated structure of Si_4C sequences, and no randomized sequences were contained in the skeleton.

Optical Properties. Figure 2 shows the UV absorption spectra of **1** (broken line), **2** (solid line), and decamethyltetrasilane (Si_4Me_{10}) (dotted line) in isooctane solutions at 295 K. All observed absorption bands are assigned to σ–σ^* excitation of the skeletons. The observed E_{max} of **2** (5.11 eV, 242.7 nm) was lower than those of **1** (6.21 eV, 199.6 nm) and Si_4Me_{10} (5.26 eV, 235.7 nm). The energy shift between **2** and Si_4Me_{10} was due to the σ-conjugation along the Si_4C-type skeleton, and this shift indicated the methylene units in the skeleton did not inhibit the interaction between neighboring silylene units. The difference between the E_{max} values of **1** and **2** means that the electronic structures of periodic polycarbosilanes depend on their periodic structures, and can be controlled by changing their sequences as previously suggested.[24]

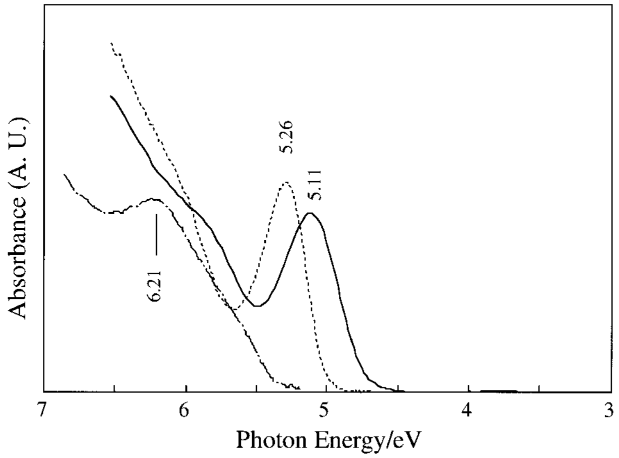

Figure 2. UV absorption spectra of **1** (broken line), **2** (solid line), and Si_4Me_{10} (dotted line) in isooctane solution at 298 K.

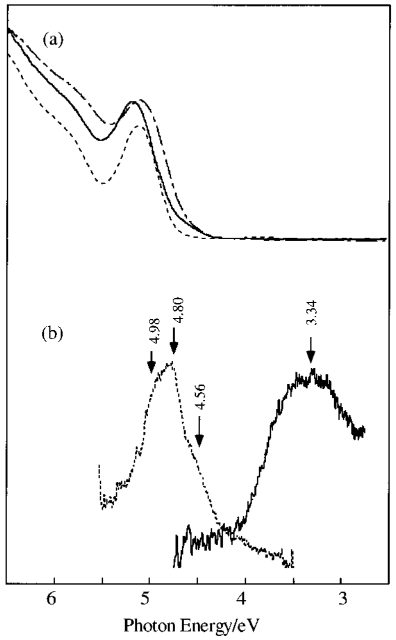

Figure 3. (a) UV absorption spectra of **2** in solid state film at 15 K (solid line) and 298 K (dotted line) and in isooctane solution at 298 K (broken line). (b) Emission spectrum excited by 4.96 eV light (dotted line) and excitation spectrum monitored by 3.4 eV light at 15 K.

Figure 3a shows the UV absorption spectra of **2** in solid-state film at 15 (solid line) and 298 K (dotted line) and in isooctane solution at 298 K (broken line), while Figure 3b shows the emission spectrum excited by 4.96 eV (250 nm) light (dotted line) and the excitation spectrum monitored by 3.4 eV (360 nm) light at 15 K. The E_{max} in the solid-state film shows an abrupt bathochromic shift from 5.15 to 5.11 eV associated with glass transition. In solid-state films, the Brownian motion of the polymer chains is more restricted than in solution, and that restriction inhibits conformations of polymers in more stable forms. Thus, this peak shift may cause the relaxation of the polymer conformation to a more stable form associated with the freezing-out of the backbone motion of the polymer chains. No peak shift was observed associated with melting, but the peak intensity increased. This change in intensity may be due to other phases whose absorption peaks are in the higher energy region, and the structural change of the 5.1-eV phase may not occur in association with melting. These thermal behaviors suggest that the 5.1-eV phase of **2** was amorphous, not crystalline. Interestingly, the absorption spectra in the solid-state film had broader profiles than that of the spectrum in solution and tailed off toward the lower region. In the lower energy region of the absorption spectrum, the excitation spectrum exhibited three peaks at 4.98 (249.3), 4.80 (258.3), and 4.56 eV (271.9 nm) as shown in Figure 3b. Each peak observed in the excitation spectrum is attributed to phases with different band-gaps.[21] Theoretical calculations on organosilane[31] and organocarbosilane[32] compounds indicate that the interaction between σ-orbitals depends on the conformation about both the Si−Si and Si−C bonds and the resulting different energy structures. Thus, the solid-state film of **2** contains several different structures in conformation, and the observed absorption spectral profile reflects this inhomogeneity. Although the exact structures of each phase cannot be identified at present, these spectral results indicate that the $\sigma-\sigma^*$ transition energy of the Si_4C-type skeleton varied least from 5.2 to 4.5 eV accompanied by conformational change. This large energy change, which is comparable to that of the representative polysilane poly(dihexylsilane)[33] means that the energy structure of the Si_4C heterocatenate strongly depends on the conformation. In addition, the large energy difference (0.7 eV) between the lowest E_{max} of **2** and that of Si_4Me_{10} indicates that the σ-conjugation in the Si_4C heterocatenate is very effective and not prevented from functioning by one carbon atom between disilanyl units. Taking into consideration the molecular weight of the repeating unit ($-Me_8Si_4CH_2-$, 284.7), we find that the DP of **2** is approximately 9 and the number of Si and C atoms in the skeleton is greater than about 40. The previous studies indicated that the $\sigma-\sigma^*$ excitation energy of Si homocatenates such as oligosilanes and polysilanes rapidly decreases as a function of chain length and reaches an almost constant value when the number of silicon atoms becomes greater than about 30.[34] Therefore, the absorption maximum of **2** is considered to reach a limiting value.

Table 1. Position of the Lowest Energy Peaks[a] in the Photoluminescence Spectra and Stokes Shifts (ΔE) of 2 and Permethyloligosilanes

compound	E_{exc}[b]	E_{emi}[c]	ΔE	condition	temp (K)	ref
2	4.56 (271.9)	3.34 (371.3)	1.22	film	15	
Si_4Me_{10}	5.37 (231.0)	3.34 (371.8)	2.03	Ar matrix	30	35[d]
Si_6Me_{14}	4.75 (261.1)	3.47 (357.1)	1.20	Ar matrix	30	35[d]
$Si_{16}Me_{34}$	3.88 (315.5)	3.93 (320.0)	0.05	3-methylpentane	77	36[d]

[a] In units of eV. Values in parentheses are in units of nm. [b] In excitation spectra. [c] In emission spectra. [d] Values converted by author.

A broad emission from **2** was observed around 3.34 eV (371.3 nm) which exhibited a strong Stokes shift. The emission intensity decreased with increasing measurement temperature, and no emission was observed above 200 K. These emission properties are similar to those of small oligosilanes rather than those of polysilanes. The emission profiles of small oligosilanes with six or fewer silicon atoms are broad and have a strong Stokes shift whereas those of ordinary polysilanes are mirror images of absorption and have only a slight Stokes shift.[35,36] Michl and co-workers explained these differences in emission properties by considering the potential surfaces of the excited states. In much longer Si homocatenates such as polysilanes, the minimum in the $^1\sigma-\sigma^*$ state is near vertical geometry, and excitation is delocalized along the skeleton (a "delocalized" exciton). As the length of the Si homocatenates is decreased, the stabilization by σ-delocalization becomes small. For small chains, the minimum is at a geometry in which one of the Si−Si bonds is stretched, and excitation is localized in a single stretched Si−Si bond (a "self-trapped" exciton), resulting in a strong Stokes shift. As shown as Figure 3b and Table 1, the emission from **2** was very broad and exhibited a strong Stokes shift similar to those of small oligosilanes. This indicates that the equivalent point of the excited state of **2** is at a geometry with a large structural change and that there is little stabilization by σ-delocalization in the excited state. Thus, the observed emission of **2** is assigned to the self-trapped exciton state.

III. Conclusion

The periodic structure of the polymer under study was confirmed by ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra. UV and PL spectroscopic studies on the optical properties revealed the nature of σ-conjugation in Si_4C heterocatenates. By increasing the number of Si units, the fundamental absorption energy became much lower than that of Si_2C-type periodic polycarbosilane. The large bathochromic shift compared to Si_4Me_{10} was due to the large interaction between σ-orbitals in the Si_4C catenate. In spite of effective σ-conjugation in Si_nC type heterocatenates, the excitation was weakly delocalized in the polymer chain unlike that of ordinary polysilanes and polygermanes. Consequently, Si_4C-type periodic polycarbosilane was shown to have a unique electronic structure in σ-conjugated polymers.

IV. Experimental Section

General Methods. All reactions were carried out with oven-dried glassware in an atmosphere of oxygen-free dry argon. All solvents were obtained from Kanto Chemical Co. (dehydrated grade) and used without further purification. Bis(chlorodimethylsilyl)methane was prepared from bis(trimethylsilyl)methane according to the reported procedure.[37] 1,2-Diphenyltetramethyldisilane was prepared by the reaction of phenyldimethylchlorosilane with sodium. Bis(trimethylsilyl)methane and phenyldimethylchlorosilane were purchased from Shin-etsu Chemical Co., and distilled just before use.

Sample films were prepared by evaporating a concentrated toluene solution on quartz substrates in a toluene-saturated atmosphere. After evaporation, the films were dried in a vacuum overnight.

^{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, and all spectra were measured at 25 °C. Mass spectra were measured on a JEOL AM150 mass spectrometer. Differential scanning calorimetry (DSC) was carried out on a Seiko DSC200 at a heating rate of 5 °C/min. UV absorption spectra and photoluminescence spectra were measured on a Hitachi U3500 spectrophotometer and an

850 fluorescence spectrophotometer, respectively. Measurement temperatures were controlled by a DAIKIN Cryo Kelvin U102CW.

Synthesis and Structural Analysis. Preparation of Bis(1-phenyltetramethyldisilanyl)methane (4). A solution of 1,2-diphenyltetramethyldisilane (28.0 g, 103.5 mmol) in THF (20 mL) was added to 1.5 g (216.1 mmol) of lithium wire in 180 mL of THF to give $Me_2PhSiLi$. The resulting $Me_2PhSiLi$ solution was added to a solution of 20.0 g (99.1 mmol) of bis(chlorodimethylsilyl)methane in 150 mL of hexane at room temperature. After 2 h of stirring, the solution was filtered and then concentrated under reduced pressure. This was followed by the dissolution of the residue in hexane, filtration, and repeated removal of the solvent. After vacuum distillation (bp 185−190 °C, 4.4 Torr), 23.5 g (39.4%) of pure **4** was isolated. Anal. Calcd for $C_{21}H_{36}Si_4$: C, 62.92; H, 9.05. Found: C, 60.8; H, 9.2. MS (EI, 70 eV) *m/e* (relative intensity) 400 (M^+ 0.3), 222 (3), 165 (100), 135 (12) ^{1}H-NMR: 7.50−7.25 (10H, $SiMe_2\mathit{Ph}$), 0.29 (12H, $Si\mathit{Me}_2Ph$), 0.05 (12H, $Si\mathit{Me}_2$), −0.27 ppm (2H, $C\mathit{H}_2$). ^{13}C-NMR: 139.67 (w), 133.76 (s), 128.24 (m), 127.68 (s) ($SiMe_2\mathit{Ph}$), −1.17 ($Si\mathit{Me}_2$), −2.68 ($\mathit{C}H_2$), −4.06 ppm ($Si\mathit{Me}_2Ph$). ^{29}Si-NMR: −16.8 ($\mathit{Si}Me_2$), −21.7 ppm ($\mathit{Si}Me_2Ph$).

Preparation of Bis(1-chlorotetramethyldisilanyl)methane (5). Compound **4** (20.0 g, 49.9 mmol) and a catalytic amount of $AlCl_3$ (0.1 g) were added to 100 mL of chloroform and stirred at 35 °C. Gaseous HCl was added to the solution until GC analysis indicated the disappearance of **4** and its monochloride. $AlCl_3$ was deactivated by the addition of acetone. After removal of the acetone−$AlCl_3$ complex, the chloroform was removed by vacuum evaporation. This was followed by the dissolution of the residue in hexane, filtration, and repeated removal of the solvent. Compound **5**, 9.9 g (62.5%), was distilled at 98−100 °C (2.3 Torr). Anal. Calcd for $C_9H_{26}Cl_2Si_4$: C, 34.04; H, 8.25. Found: C, 41.1; H, 9.6. MS (EI, 70 eV) *m/e* 281 (3), 223 (100), 173 (11), 165 (17), 151 (15), 145 (53), 129 (37), 113 (17). ^{1}H-NMR: 0.48 (12H, $Si\mathit{Me}_2Cl$), 0.23 (12H, $Si\mathit{Me}_2$), −0.04 ppm (2H, $C\mathit{H}_2$). ^{13}C-NMR: 1.95 ($Si\mathit{Me}_2Cl$), −1.83 ($Si\mathit{Me}_2$), −3.63 ppm ($\mathit{C}H_2$). ^{29}Si-NMR: 23.4 ($\mathit{Si}Me_2Cl$), −16.06 ppm ($\mathit{Si}Me_2$).

Preparation of Poly[(octamethyltetrasilylene)methylene] (2). A total of 9.0 g (28.3 mmol) of **5** was added dropwise to 100 mL of toluene containing 1.6 g (67.9 mmol) of dispersed sodium and 1.0 g (4.5 mmol) of 15-crown-5. After 8 h of reflux, the reaction mixture was filtered, and the filtrate was poured dropwise into the excess methanol. The resulting polymer was purified twice by reprecipitation from the toluene solution with methanol, giving 250 mg of **2** as a white waxy solid (yield: 7.3%). Anal. Calcd for $C_9H_{26}Cl_2Si_4$: C, 43.83; H, 10.63. Found: C, 41.4; H, 10.3.

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